# SOURCES AND CONTROLS OF REACTIVE NITROGEN GAS EMISSIONS FROM A MOJAVE DESERT ECOSYSTEM

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# SOURCES AND CONTROLS OF SOIL EMISSIONS OF REACTIVE NITROGEN GASES FROM A MOJAVE DESERT ECOSYSTEM

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This body of work considerably expands our understanding of gaseous nitrogen (N) loss dynamics in arid ecosystems, a process that directly affects long-term N bioavailability and the release of chemically important gas species into the atmosphere. Chapter one focuses on identifying controls over biological sources of reactive N gas emissions, especially the pulse of NO and $NH_3$ that occurs following precipitation. This research shows a two-step response of reactive N gas emissions to pulsed water additions. First, there is a large transient $NH_3$ pulse. Second, biological activity is stimulated leading to NO production by nitrifying bacteria. Results indicate that biological sources of NO and $NH_3$ efflux respond primarily to the addition of water; however, fluxes are modulated by temperature and nutrient constraints on microbial activity. Chapter two explores the role of non-biological processes in reactive N gas emissions from desert soils. Combination of laboratory and field measurements show that abiotic reactions are a key component of N loss from desert soils, both under dry conditions and during post-wetting periods. It is hypothesized that during the summer, extreme surface soil temperatures caused by direct exposure to incoming solar radiation result in thermal decomposition of N-containing compounds, yielding elevated rates of reactive N gas efflux. Chapter three focuses on the effects of elevated $CO_2$ on soil fluxes of reactive N gases. Under soil conditions optimal for biological activity, long-term fumigation with elevated $CO_2$ reduces

reactive N gas losses in the islands of fertility created by the dominant shrub *Larea tridentata*. These results provide supporting evidence that elevated $CO_2$ alters soil N dynamics in arid ecosystems, including increased N immobilization and decreased N mineralization and nitrification. Chapter four provides a robust estimate of annual reactive N gas emissions for a Mojave Desert ecosystem, accounting for daily, seasonal and yearly variation in environmental conditions. This annual estimate of 0.1 to 0.6 kg N $ha^{-1}$ $y^{-1}$ includes considerable variation, reflecting inter-annual variability in summer precipitation and growing season moisture conditions. These results demonstrate the strong impact that alterations in precipitation patterns under future climate scenarios will have on N dynamics in water limited ecosystems.

## BIOGRAPHICAL SKETCH

Carmody (Carrie) McCalley grew up in Palo Alto, CA with her parents and older brother Roddy. Her parents starting taking her backpacking in at the early age of 2 and although she initially hated it, she came to love hiking and mountain climbing, developing a love of, and interest in, the great outdoors. Her parents also encouraged her interest in science, which was strengthened by many teachers throughout elementary, middle and high school. Carrie graduated from Henry M. Gunn High School in 1999.

Carrie went on to earn a bachelor's degree in biology at Middlebury College in Vermont. At Middlebury, Carrie pursued her interests in biology where she was mentored by many excellent professors. She particularly enjoyed the ecology courses taught by Sallie Sheldon and Andrea Lloyd, which convinced her that she wanted to become a scientist and conduct environmental research. While at Middlebury Carrie also, much to her surprise, found that she enjoyed studying Chemistry and added a minor in the subject.

During her junior year at Middlebury, Carrie spent the fall semester at the Marine Biological Laboratory, participating in the Semester in Environmental Science (SES) program at the Ecosystem Center. This program introduced her to the field of biogeochemistry, which combined her interests in ecology and chemistry. When she returned to Middlebury, Carrie knew that she wanted to pursue a research career in biogeochemistry and started preparing for this future by conducting a senior thesis project titled "The effect of species composition and stand age on nitrogen dynamics in northern hardwood forests."

The summer after her junior year in college Carrie went to northern Alaska as part of the Research Experience for Undergraduates (REU) program. She worked at the Toolik Lake Field Station as part of the terrestrial ecology research group headed

by Gus Shaver. While in Alaska she worked on a project measuring N-fixation in an arctic tundra ecosystem. After she graduated from Middlebury in 2003, she went to work full-time for Gus Shaver as a research assistant. This job provided her with valuable research experience working on several projects that included fieldwork in both Alaska and Sweden.

Carrie then started a graduate program at Cornell University in the Department of Ecology and Evolutionary Biology working with Jed Sparks. During her time at Cornell Carrie spent countless hours in the Mojave Desert working at the Nevada Test Site measuring reactive nitrogen gas fluxes. More recently her research has also taken her to Moab, UT, where measuring gas fluxes is much more picturesque. In addition to her own research, Carrie has also participated in other projects while at Cornell, which have given her the opportunity to work in ecosystems ranging from forests to cabbage fields.

To my parents

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I have many, many people to thank for the fact that I not only learned a tremendous amount while at Cornell, but also really enjoyed my time as a graduate student. To start off, I want to thank my advisor, Jed Sparks. Jed taught me many skills that will serve me well throughout my career, the art of constructing a scientific talk and well written paper, how to be calm in the face of catastrophic instrument failure, and other practical skills ranging from soldering to electrical wiring. He shared with me his love of deserts and much to my surprise got me hooked on studying these fascinating ecosystems.

I had two other, great committee members, Peter Groffman and Tim Fahey, who made both my 'A' and 'B' exams a relatively pleasant experience and provided excellent feedback, particularly on the final chapter of my dissertation.

None of this research would have been possible without the help and friendship of Kim Sparks, who taught me many things both in the lab and in the field and who introduced me to the perfect field sandwich (bagel and cream cheese with salami, which always tastes good in the desert, no matter what the weather). In addition to Kim and Jed, many other members of the Sparks lab joined me in the field. Allyson, Brian, Danica, and John thank you so much for coming out to the desert with me and for being good humored about sitting on a platform in all kinds of weather turning valves all day!

Throughout my time at Cornell, the Sparks' lab and EEB department have been a great source of friendship and support. I want to thank Allyson Eller for being a fantastic friend, skiing companion, and source of ideas for how to do things better and source of sympathy when things didn't work out as planned. Dena Vallano, Danica Lombardozzi, Kirsten Coe, and Brian Strahm you guys were great and remarkably willing to listen to the same practice talk, research idea etc… over and over again. I

also want to thank April Melvin, Dave Baker, Krista Capps and many, many other EEB grad students for making graduate school so much fun.

In addition to the EEB faculty and graduate students, many members of the staff provided invaluable help as I worked on my dissertation. Dee Dee and Luanne patiently answered my financial questions, while Carol and Janeen were always friendly and helpful, even when I had the most inane questions. Finally, much of my research would not have been possible without Gary's assistance in constructing all sorts of odd things and his patience with me filling his shop with PVC shavings as I beveled countless soil collar edges.

I want to thank many family members and friends, especially my parents who have always been there for me and have been a source of inspiration all my life. The Lindenburg and Hock families, who have both acted as my 'east coast family'. Allison Nagel, I couldn't ask for a better friend and I could never have done all my research without your willingness to dog-sit for weeks at a time. I also want to thank my dog Colby for reminding me to get outside and go for a run, even in the busiest, most stressful times and Susan Wiser, Cayuga Dog Rescue and the many foster dogs that came through my house for providing a great distraction from working on my thesis.

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CHAPTER 1

# CONTROLS OVER NITRIC OXIDE AND AMMONIA EMISSIONS FROM MOJAVE DESERT SOILS[1]


## Abstract

Emissions of reactive N compounds produced during terrestrial N cycling can be an important N loss pathway from such ecosystems. Most measurements of this process focus on NO and $N_2O$ efflux, however, in alkaline soils such as those in the Mojave Desert, $NH_3$ production can be an important component of N gas loss. We investigated patterns of NO and $NH_3$ emissions in the Mojave Desert and identified seasonal changes in temperature, precipitation and spatial heterogeneity in soil nutrients as primary controllers of soil efflux. Across all seasons, $NH_3$ dominated reactive N gas emissions with fluxes ranging from 0.9 to 10 ng N $m^{-2}$ $s^{-1}$ as compared to NO fluxes of 0.08 to 1.9 ng N $m^{-2}$ $s^{-1}$. Fluxes were higher in April and July than in October, however, a fall precipitation event yielded large increases in both NO and $NH_3$ efflux. To explore the mechanisms driving field observations, we combined NO and $NH_3$ soil flux measurements with laboratory manipulations of temperature, water and nutrient conditions. These experiments showed a large transient $NH_3$ pulse (~70 - 100 ng N $m^{-2}$ $s^{-1}$) following water addition, presumably driven by an increase in soil $NH_4^+$ concentrations. This was followed by an increase in NO production, with maximum NO flux rates of 34 ng N $m^{-2}$ $s^{-1}$. Our study suggests that immediately following water addition $NH_3$ volatilization proceeds at high rates due to the absence of microbial competition for $NH_4^+$; during this period N gas loss is insensitive to changes in temperature and soil nutrients. Subsequently, NO emission increases and



[1] First published as McCalley, C.K. and J.P. Sparks. 2008. Controls over nitric oxide and ammonia emissions from Mojave Desert soils. Oecologia **156**: 871-881. The original publication is available at http://www.springerlink.com/content/tn178t0p85nt2787/?p=e9beb0423fd347ebba40c57b33036c92&pi=13

rates of both NO and $NH_3$ emission are sensitive to temperature and nutrient constraints on microbial activity. Addition of labile C reduces gaseous N losses, presumably by increasing microbial immobilization, whereas addition of $NO_3^-$ stimulates NO and $NH_3$ efflux.

**Introduction**

In the presence of sufficient water, N is thought to limit productivity in many arid environments, however, our understanding of the processes that control N availability in these systems is still limited (Verstraete and Schwartz 1991). Relative to internal storage and turnover, N losses from deserts are small (Rundel and Gibson 1996), yet understanding these fluxes are intrinsic to the understanding of long-term ecosystem N dynamics. In comparison to other terrestrial environments, N loss mechanisms such as leaching are typically small in deserts. For example, fluxes for the Mojave Desert have been approximated at < 2 kg N $ha^{-1}$ $yr^{-1}$ for leaching and erosion losses combined (Rundel and Gibson 1996). This means that in such environments, understanding gaseous emissions will be necessary for closure of the nitrogen cycle.

To date, studies have focused on measuring emissions of NO and $N_2O$ to quantify gaseous N loss from soils, however, many arid environments have highly alkaline soils, meaning that $NH_3$ volatilization may be an important and largely unstudied N loss term (Dawson 1977, Schaeffer et al. 2003). Measurements in the Mojave Desert indicate $N_2O$ efflux is highly variable both spatially and temporally and is unlikely to be a substantial form of N loss (Billings et al. 2002) and NO and $NH_3$ emissions are predicted to dominate trace N gas fluxes. Multiple studies have identified nitrification and denitrification as sources of NO (eg. Davidson et al. 1993; Firestone and Davidson 1989; Parton et al. 2001; Skiba et al. 1993), with fluxes

regulated by factors that include the concentration of inorganic N ($NO_3^-$ and $NH_4^+$), soil moisture, temperature, accessibility of labile C, and physical soil properties (Skiba et al. 1993, Hall et al. 1996, Parton et al. 2001). Similar to NO production from nitrification, rates of $NH_3$ volatilization should be sensitive to soil conditions that influence $NH_4^+$ concentrations and turnover in the soil (Nelson 1982, Schlesinger and Peterjohn 1991). Given this overlap in substrate use between nitrification and $NH_3$ volatilization, it is important to not only quantify rates and controls over $NH_3$ production from desert soils, but also identify the relationships between soil fluxes of $NH_3$ and NO.

Turnover of N in arid ecosystems is characterized by brief periods of intense biological activity following precipitation events (Noy-Meir 1973, Austin et al. 2004, Belnap et al. 2005). Rates of N cycling during these periods are controlled by abiotic factors, especially temperature, as well as soil nutrient availability (Gallardo and Schlesinger 1995, Fernandez et al. 2006). Arid environments have high spatial heterogeneity in soil resources, resulting in variation in N dynamics across the landscape, with patterns often associated with the accumulation of soil nutrients beneath shrubs (Schlesinger et al. 1996).

In addition to being sensitive to the size and composition of the soil N pool, microbial transformations of N also depend on C availability. Carbon provides fuel for heterotrophic microbial processes including N mineralization and immobilization and therefore natural variations in soil C as well as C additions have been shown to influence soil N dynamics (Gallardo and Schlesinger 1995, Zaady et al. 1996, Schaeffer et al. 2003). It is clear that carbon, nitrogen, and water availability influence N transformations that lead to production of N gases, what remains unclear is whether these factors exert similar controls over both NO and $NH_3$ emission and whether our

understanding of NO efflux from less alkaline systems still hold in systems with high rates of $NH_3$ volatilization.

The field component of this study was designed to characterize the role of reactive N gas emissions in desert N cycling, specifically addressing the relative importance of NO and $NH_3$ efflux. These measurements provided us with baseline data on temporal and spatial variation in the size and composition of reactive N gas efflux. In the laboratory, we focused on the response of NO and $NH_3$ emissions to a simulated rain event and examined how changing temperature, C and N availability altered this response. We hypothesized that (1) emissions of both NO and $NH_3$ would increase following water addition and fluxes would remain elevated for several days, however, the magnitude and timing of this response would be different for the two gas species, (2) the direct role of biological processes, nitrification and denitrification, in NO production as compared to the indirect role of biological processes in $NH_3$ production would result in NO efflux being more sensitive to temperature, with higher NO fluxes occurring at higher temperatures, and (3) NO and $NH_3$ emissions following water addition would increase with the addition of N and decrease with the addition of C due to similar responses to changes in N mineralization and immobilization. In addition, we predicted that the higher resource availability in "islands of fertility" associated with the dominant shrub *Larrea tridentata* (Romney et al. 1980, Titus et al. 2002) would yield consistently higher rates of NO and $NH_3$ efflux. In contrast, lower resource availability in interspace soils should make effluxes from these areas generally lower and more sensitive to changes in nutrient conditions.

## Methods

*Study Site*

Field measurements and soil collections were conducted at the Mojave Global Change Facility (MGCF) located in Nye County, Nevada (36°49'N, 115°55'W), 90 km northwest of Las Vegas, NV USA at an elevation of 970 m. The site lies within the Nevada Test Site (NTS), administered by the USA Department of Energy (DOE) and has been protected from recreation and grazing disturbances for approximately 50 years (Jordan et al. 1999). Mean annual rainfall is 140 mm and precipitation occurs primarily as winter storms and as short, localized summer events. Temperatures range from winter minima of -10°C to summer temperatures > 47°C. The site is a *Larrea tridentata – Ambrosia dumosa* plant community and has intact biological soil crusts covering ~20% of the soil surface (Titus et al. 2002). Soils are Aridsols derived from calcareous alluvium with a loamy sand texture (89% sand, 6% silt and 5% clay). Subsoils lack a caliche layer, resulting in well-drained soils. Soil pH at the site ranges from 9-11 (Evans unpublished data) and soils are spatially heterogeneous in nutrients, texture and infiltration (Romney et al. 1980).

*Field Measurements*

Field measurements were made using soil collars, these collars were 25.5 cm diameter, 15 cm tall, and were installed approximately 7.5 cm into the soil profile in June 2004. There were a total of 16 soil collars, 4 in each of the following cover types: under the evergreen shrub *Larrea tridentata* (creosote bush), under the $C_4$ bunchgrass *Pleuraphis rigida* (big gaelleta), soil interspace with visible biological soil crust, and soil interspace with no visible crust. Visibility of the biological soil crust was determined qualitatively by the presence or absence of lichen and moss. Instantaneous flux measurements of NO, $NO_y$ (all oxidized forms of nitrogen) and

$NH_3$ were made once in each collar during 2-week periods in October 2004, April 2005, and July 2005 (only 10 collars were sampled in April and 12 in October). All measurements were made between mid-morning and late-afternoon. In addition to background flux measurements, a large natural rain event (37.8 mm) in October 2004 enabled us to make pre and post-rain event measurements (fluxes were measured in 3 collars per cover type prior to the rain event and all 16 collars after the rain event). Due to logistical constraints, the post-rain event measurements were spread across several days and each collar was sampled once during a six-day period.

*Soil Profile Collection*

Intact soil profiles were collected April 17, 2005 in areas with visible biological soil crust, no visible biological soil crust and soils beneath *Larrea tridentata*. Eight soil profiles were collected in each soil type. PVC pipes measuring 25.5 cm in diameter and 15 cm in depth were driven 7.5 cm into the ground using a rubber mallet. They were then excavated such that a stiff canvas cloth could be placed under the piping, ensuring the integrity of the profile. The soil cores were then placed in plastic tubs filled with 3 – 5 cm of sand, installed in a custom designed transport container and driven with minimal disturbance to Cornell University where they were stored in a greenhouse at 21°C. After arrival at Cornell, paraffin wax was used to seal the sand surface surrounding the PVC encased soil profile. This set-up allowed a system where water could drain naturally from the profile and collect in the sand below.

*Laboratory Incubations*

We conducted two laboratory incubation experiments in growth chambers (Conviron, CMP 3244). Environmental conditions for both experiments were 12 hr

daylength, photosynthetically active radiation of 350 μmol $m^{-2}$ $s^{-1}$, and 20% relative humidity. One month prior to the first set of experimental measurements, the soil profiles were moved from the greenhouse and into the growth chambers where half were incubated at 17.5 °C and half at 35 °C.

At the time of measurement, each profile received distilled water in the form of a 20 mm rain event and NO and $NH_3$ flux measurements were made before (Day 0), within 30 minutes of watering (Day 1), and 1, 2 and 5 or 6 days after the water addition.

The soil cores were then stored in a greenhouse (21 °C) for 3 months before a second laboratory incubation experiment was conducted. One month prior to the second experiment all cores were transferred to growth chambers and incubated at 35 °C. Again each core received a 20 mm rain event, however this time half of the cores also received a N addition in the form of 20 μg $KNO_3$-N $g^{-1}$ dry soil, approximately 5 times the ambient concentration of inorganic N in the soil, and the other half received a C addition in the form of 400 μg dextrose-C $g^{-1}$ dry soil. Nutrient addition amounts were calculated using an average dry mass per soil core of 7 kg and additions were based on concentrations used by Schaeffer et al. (2003) when measuring N cycling responses of Mojave Desert soils to nutrient additions. NO and $NH_3$ flux measurements were made before (Day 0), within 30 minutes of watering (Day 1), and 1, 2 and 5 or 6 days after the water and nutrient addition.

*Reactive N Gas Flux Measurements*

Nitrogen gas fluxes (NO, $NO_y$, and $NH_3$) were measured using selective thermal and chemical decomposition converters to reduce or oxidize all reactive nitrogen trace gases (e.g., oxidized forms and ammonia) to NO. During measurement, a sealed top constructed of UV-transparent material (FEP Teflon) was placed over the

collar. The collar top had two Teflon ports and a small mixing fan to ensure natural turbulent conditions within the collar. This system is open to the atmosphere, which minimizes induced pressure differences associated with chamber based measurement techniques.

To make a measurement, outside air is passed, at 1 L $min^{-1}$, through a large-volume (750 mL) charcoal filter to scrub out reactive N and then through the collar and into the measurement system. Air concentrations of reactive N at the time of measurement were < 0.5 ppb NO and < 2 ppb $NH_3$ making it unlikely that changes in the diffusion gradients caused by scrubbing incoming air were large enough to alter soil fluxes. The measurement system consists of two conversion cells that reduce $NO_y$ (total oxidized N) and total reactive N ($NO_y$ + $NH_3$) to NO, respectively, and a chemiluminescence NO detector. Each converter can be isolated by Teflon valves and independent measurements can be made for NO (no conversion), $NO_y$ ($NO_y$ converter only), and total reactive N ($NH_3$ + $NO_y$ conversion). Fluxes were calculated based on steady-state concentrations using the equation C * q/A where C is concentration (nmol $L^{-1}$), q is the flow rate (L $s^{-1}$) and A is area ($m^2$) of the soil surface and $NH_3$ fluxes were calculated by subtracting the $NO_y$ flux from the total reactive N flux. Measurements of NO, $NO_y$ and $NH_3$ were made sequentially and total measurement time averaged 20-30 min. The $NH_3$ conversion cell consists of a 30 cm length of nickel-chromium alloy tubing (INCONEL 600) passed through a mini tube furnace (Barnstead International, Model F21125) heated to 825 ˚C. Laboratory calibrations of the converter have shown 86% conversion efficiency for $NH_3$ with no influence on NO concentration. The $NO_y$ converter is a heated glass catalytic converter that contains a 60-cm piece of ¼" gold tube heated to 300°C. A small flow of $H_2$ (30 mL $min^{-1}$) is introduced just prior to the heated region to facilitate the reduction of oxidized N to NO. Laboratory calibration tests have shown a 100% conversion of

$NO_2$ and HONO and conversion efficiencies between 78 – 99% for other components of $NO_y$ (i.e., peroxyacetyl nitrate, alkyl nitrate, $HNO_3$ and other forms of $NO_y$ usually formed in the atmosphere).

After conversion (or directly in the case of the NO only measurement), air is passed through an NO analyzer (Ecophysics, Model CLD 770). The CLD 770 detects light from the chemiluminescence reaction between NO and $O_3$:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\upsilon$$

The analyzer avoids interferences (a common problem with many NO analyzers) using a pre-reaction chamber where $O_3$ is used to consume NO before entering the reaction chamber. Because the rate of reaction with NO is very fast and the reaction with most interference compounds is relatively slower, two sequential runs (the first utilizing the pre-reaction cell and second going directly to the sample cell without pre-reaction) allows for the quantification of NO independent of all interferences and gives instrument a detection limit of 50 pptv. The instrument was calibrated by sequential dilution of an NO standard (Scott Specialty Gases, Irvine, CA) daily.

*Statistical Analysis*

We used analysis of variance (PROC MIXED, SAS 9.1) with a Tukey post hoc test to determine the effects of season, cover type, and precipitation on field fluxes of NO and $NH_3$ as well as the effects of temperature, cover type and water/nutrient addition on NO and $NH_3$ fluxes through time under laboratory conditions. All analyses were performed using SAS statistical software (Cary, NC). Statistical significance was determined at $\alpha = 0.05$. Errors are presented as ±1 SE.

**Results**

Ammonia and NO fluxes from dry soils varied significantly with season, $NH_3$ fluxes were significantly higher in April than in either October ($p = 0.02$) or July ($p = 0.04$), while NO fluxes were significantly lower in October than in either April ($p = 0.002$) or July ($p = 0.006$) (Figure 1.1). Variation in fluxes among cover types did not influence seasonal patterns; therefore cover types were pooled for clarity. Total losses of reactive N in the spring were double those measured in the fall and although NO fluxes were elevated in the summer overall summer N gas losses were only marginally larger than those measured in the fall. Ammonia was the dominant reactive N gas species emitted from dry soils. Ammonia fluxes ranged from 0.9 to 10 ng N $m^{-2}$ $s^{-1}$ whereas NO fluxes were smaller, with values ranging from 0.08 to 1.6 ng N $m^{-2}$ $s^{-1}$.

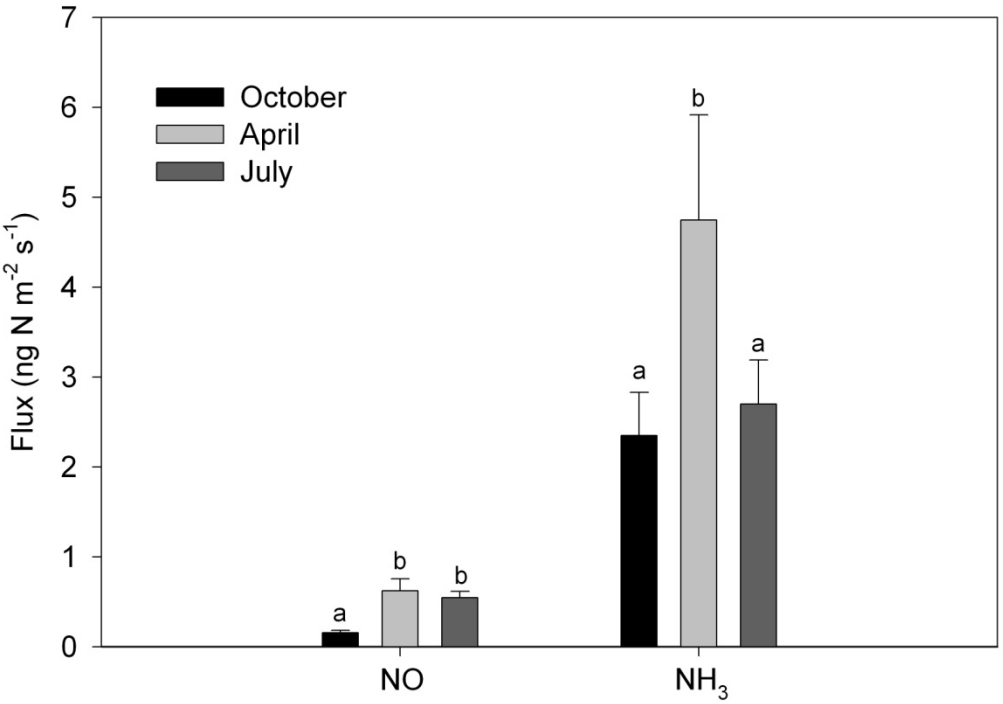


**Figure 1.1** Seasonal patterns of NO and $NH_3$ efflux from dry Mojave Desert soils (letters indicate significant differences between flux measurements for a particular gas species).

Following a natural rain event there was a significant increase in soil fluxes of NO ($p = 0.002$) and $NH_3$ ($p < 0.0001$) (Figure 1.2). Increases in soil emissions were

substantial; post-rain NO and $NH_3$ fluxes were 8 to 40 and 5 to 10 times higher than pre-rain fluxes, respectively. There was a significant rain by cover type interaction for NO efflux ($p = 0.02$); post-rain fluxes of NO were significantly higher in soils under *Larrea tridentata* than in soils from the other cover types ($p = 0.0009$). Similar to dry soils, $NH_3$ dominated post-rain reactive N gas fluxes, with four times higher efflux as compared to NO.

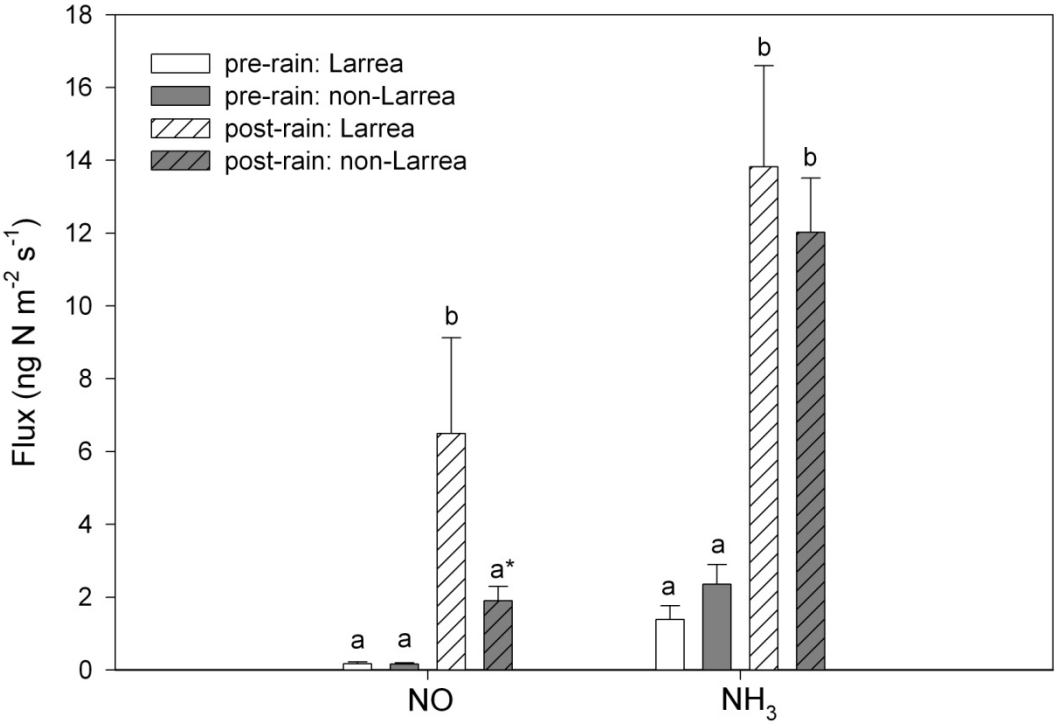


**Figure 1.2** Soil NO and $NH_3$ fluxes before and after a natural rain event in the Mojave Desert (letters represent significant differences between flux measurements within a gas species, the asterisk above the non-*Larrea* post-rain NO flux indicates that there is a trend ($p = 0.07$) towards a difference between pre and post-rain values).

Under laboratory conditions, temperature had an opposing effect on NO compared to $NH_3$ emission from dry soils (Figure 1.3). In all soils, NO emissions were higher from soils incubated at 35°C compared to 17.5°C ($p < 0.04$) whereas $NH_3$ emissions were significantly higher at 17.5°C from crust soils ($p = 0.001$) and there was a trend towards this pattern in non-crust soils ($p = 0.1$). At both incubation temperatures, $NH_3$ efflux was higher than NO efflux. This difference was particularly

pronounced at 17.5 °C, where soil fluxes of $NH_3$ were more than ten times greater than NO fluxes. In contrast, at 35 °C there was only a 1.5 to 2 fold difference between $NH_3$ and NO efflux. In terms of overall magnitude of emission, interspace soils (crust and no crus1t soils) exhibited nearly double the total reactive N gas fluxes at 17.5 °C compared to those measured at 35 °C. In contrast, emissions from soils derived from under *Larrea tridentata* were similar (~5 - 6 ng N $m^{-2}$ $s^{-1}$) regardless of temperature.

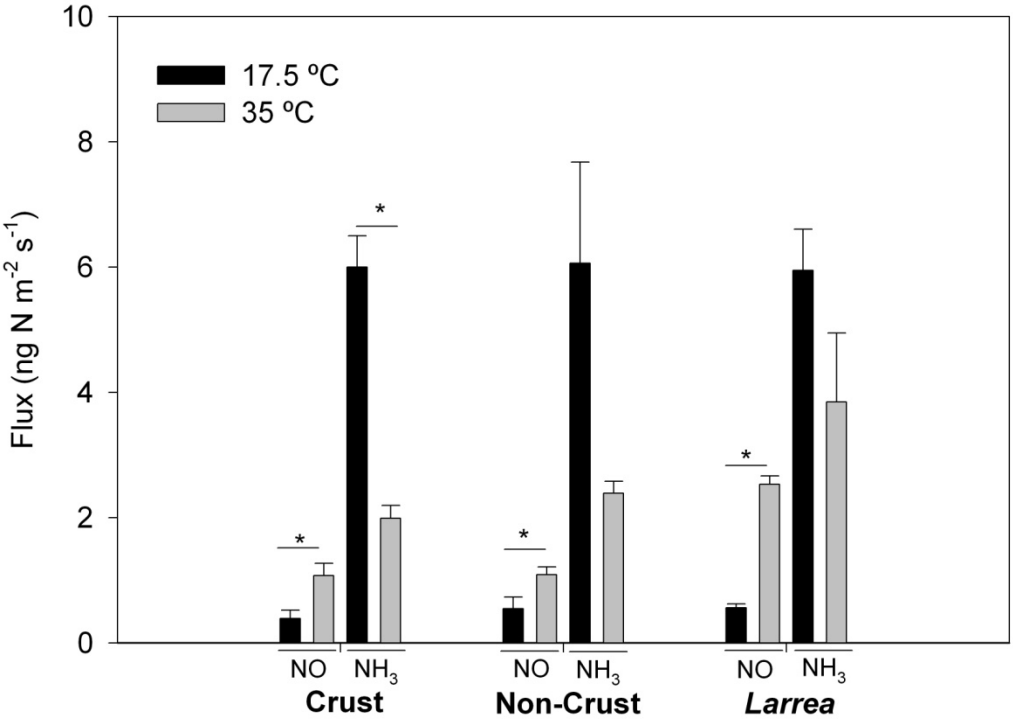


**Figure 1.3** The effect of temperature and cover type on NO and $NH_3$ efflux from dry Mojave Desert soil (asterisks indicate a significant differences between 17.5 °C and 35 °C).

The addition of water to soil profiles caused significant changes in emissions of NO ($p < 0.0001$) and $NH_3$ ($p < 0.0001$) (Figure 1.4). Immediately following water addition (day 1), there was a large, transient $NH_3$ pulse. This pulse was particularly pronounced in crust and non-crust soils where fluxes averaged 94 and 70 ng N $m^{-2}$ $s^{-1}$, respectively. NO fluxes also increased following water addition; however, this response was delayed relative to the $NH_3$ response, with fluxes peaking one to two

days after the addition of water. Peak post-water fluxes of NO were highest in *Larrea* soils; with maximum NO effluxes of 34 ng N $m^{-2}$ $s^{-1}$ as compared to 18 ng N $m^{-2}$ $s^{-1}$ in interspace soils.

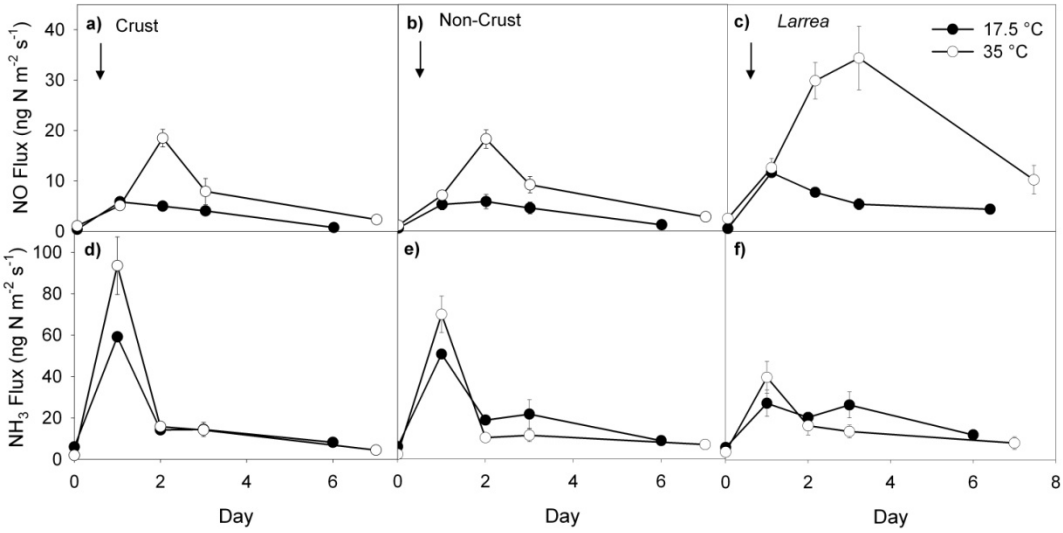


**Figure 1.4** Response of NO and $NH_3$ efflux to a pulse water addition at two temperatures (20 mm water addition is indicated by arrows). **(a,d)** flux from soils with a visible biological soil crust, **(b,e)** flux from soils with no visible biological soil crust, **(c,f)** flux from soils collected beneath *L. tridentata*.

There were significant interactions between the response of reactive N gas emissions to soil wetting, cover type ($p < 0.0001$) and incubation temperature ($p < 0.0001$) (Figure 1.4). Crust and non-crust soils had similar patterns of NO and $NH_3$ efflux following water addition and this response was different from that observed from *Larrea* influenced soils. The $NH_3$ pulse observed immediately following soil wetting was substantially higher in interspace soils as compared to *Larrea* influenced soils, with interspace fluxes approximately double those measured from *Larrea* soils. Nitric oxide efflux showed the opposite pattern, with peak fluxes from *Larrea* soils being double those measured from interspace soils. All cover types exhibited similar responses to increasing temperature from 17.5 °C to 35 °C, with higher incubation temperature yielded higher post-water fluxes of both $NH_3$ and NO. Temperature had a

particularly strong effect on post-water NO efflux, peak NO fluxes from soils incubated at 35 °C were 3 times those from soils incubated at 17.5 °C.

Carbon (dextrose) and N ($KNO_3$) had a significant effect on post-wetting fluxes of NO ($p < 0.0001$) and $NH_3$ ($p < 0.0001$) (Figure 1.5). Nitrogen addition stimulated both NO and $NH_3$ efflux in all soils, prolonging the period of elevated $NH_3$ emissions from one to several days and more than doubling the maximum NO efflux for all cover types. In contrast, C addition caused a dramatic reduction in reactive N gas emissions, especially from crust and non-crust soils.

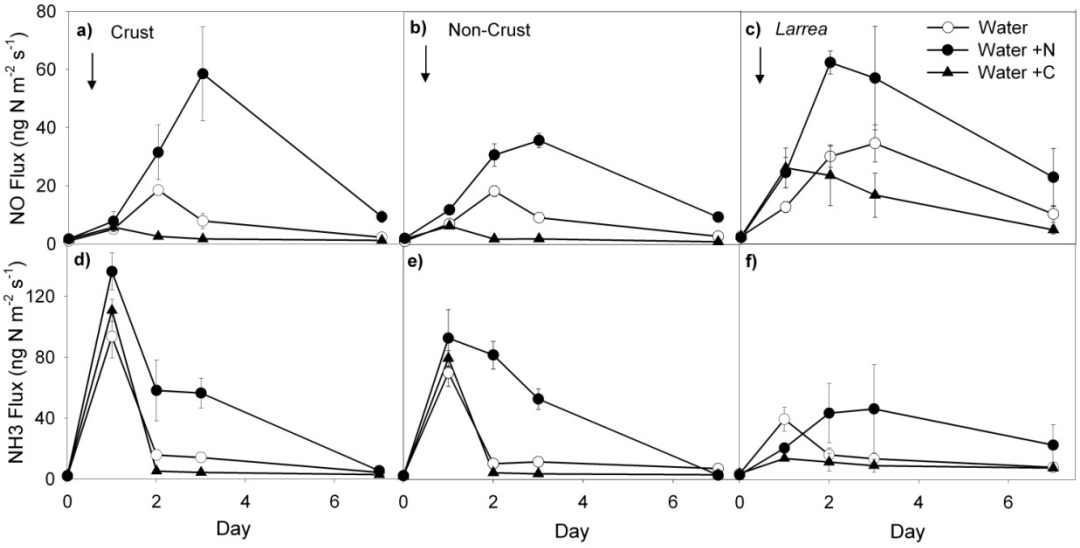


**Figure 1.5** The influence of C and N availability on the response of NO and $NH_3$ efflux to a pulse water addition (20 mm water addition is indicated by arrows). **(a,d)** flux from soils with a visible biological soil crust, **(b,e)** flux from soils with no visible biological soil crust, **(c,f)** flux from soils collected beneath *L. tridentata*.

As with the water addition, crust and non-crust soils showed a similar response to nutrient additions, while *Larrea*-influenced soils responded differently. The effect of cover type is apparent when comparing the response of soil NO efflux to labile C additions (Figure 1.5, closed triangles). In crust and non-crust soils, treatment with C virtually eliminated the post-water NO pulse and caused $NH_3$ emissions to rapidly return to baseline levels following the simulated rain event. In contrast, treatment of *Larrea* soils with labile C did not have a large effect on the magnitude of NO or $NH_3$

emissions, however, it did cause a shift in the timing of the response, with fluxes peaking on day 1 instead of day 3.

**Discussion**

This study simultaneously quantified soil emissions of NO and $NH_3$ and indicated that in alkaline soils, such as those found in the Mojave Desert, $NH_3$ is the dominant form of reactive trace N gas loss. Our estimates of $NH_3$ volatilization also suggest that the acid trap method employed in previous studies underestimate instantaneous $NH_3$ emissions. Field fluxes of $NH_3$ from dry soils were 1.5 – 3.5 times those measured by Billings et al. (2002) and were similar in magnitude to those measured in wet soils by Schaeffer et al. (2003). Additionally, our range of post-wetting $NH_3$ pulses of ~ 28 – 140 ng N $m^{-2}$ $s^{-1}$ were comparable to the maximum pulse of ~ 112 ng N $m^{-2}$ $s^{-1}$ reported in Schaeffer and Evans (2005) for the Colorado Plateau.

Nitric oxide flux estimates of 0.14 – 2.5 ng N $m^{-2}$ $s^{-1}$ from dry soils in this study fall within the range of measurements reported for other arid and semi-arid environments. Measurements from semi-arid grassland and shrubland sites range from 0.2 – 2.8 ng N $m^{-2}$ $s^{-1}$ (Smart et al. 1999) and 2.6 – 5.7 ng N $m^{-2}$ $s^{-1}$ (Martin et al. 1998) for shortgrass steppe ecosystems and 0.4 – 8.7 ng N $m^{-2}$ $s^{-1}$ across a mesquite gradient (Martin et al. 2003). In the Chihuahuan Desert, Hartley and Schlesinger (2000) measured fluxes of < 0.3 ng N $m^{-2}$ $s^{-1}$ in the dry season and 0.3 – 97 ng N $m^{-2}$ $s^{-1}$ during the wet season. Wetting of Mojave soils produced an NO pulse ranging from ~7 – 35 ng N $m^{-2}$ $s^{-1}$, similar to pulses of 37 and 14 ng N $m^{-2}$ $s^{-1}$ from grassland and shrubland soils, respectively, in the Chihuahuan Desert. When looking at NO flux estimates for a range of natural ecosystems, fluxes from the Mojave Desert are larger than or comparable to estimates for temperate forests, comparable in magnitude to several flux estimates from dry soils in tropical forests and savannas (Johansson et al.

1988, Sanhueza et al. 1990, Davidson et al. 1991, Rondon et al. 1993), and lower than estimates from more mesic tropical forest and savanna ecosystems (Johansson et al. 1988, Johansson and Sanhueza 1988, Cardenas et al. 1993, Serca et al. 1994). The peak NO pulses measured in our laboratory experiment were lower than the approximately 140 ng N $m^{-2}$ $s^{-1}$ NO pulse measured by Davidson et al. (1993) in a seasonally dry tropical forest in Mexico or the 150 – 250 ng N $m^{-2}$ $s^{-1}$ post-rain flux measured by Johansson and Sanhueza (1988) in a tropical savanna. However, the combined NO + $NH_3$ pulse (39 – 112 ng N $m^{-2}$ $s^{-1}$) following wetting of Mojave soil in our study suggests that pulse rain events in arid environments, especially those with high alkalinity, lead to total losses of reactive N gases comparable to other systems.

The seasonal measurements of NO and $NH_3$ fluxes collected under ambient soil conditions in this study can be used to develop an estimate of the contribution of N gas emission to the annual N budget in the Mojave Desert. Assuming that each of the 3 seasons measured in this study represent one quarter of the total year, with the fourth quarter being winter months whose N gas production is likely to be minimal (estimated at ½ the N gas flux measured in October), then N gas losses in the form of NO and $NH_3$ are ~ 1 kg N $ha^{-1}$ $yr^{-1}$, with $NH_3$ comprising ~90% of the flux. If you factor in the considerably larger N gas pulses that occur following precipitation an additional 0.4 – 0.6 kg N $ha^{-1}$ $yr^{-1}$ (30 – 45 days of elevated fluxes) is lost as NO and $NH_3$. Rundell and Gibson (1996) working at a similar site in the Mojave Desert estimated plant uptake at ~ 4.5 kg N $ha^{-1}$ $yr^{-1}$ and erosion losses (including leaching) at < 2 kg N $ha^{-1}$ $yr^{-1}$. These numbers suggest ~ 30-40 % of the loss of nitrogen from this system could be in the form of gaseous NO and $NH_3$.

In addition to providing an estimate of the contribution of NO and $NH_3$ efflux to N losses from Mojave Desert soils, the field measurements in this study enabled us to develop general characterizations of the pattern of reactive N loss from an intact

arid ecosystem. Measurements made over multiple seasons suggest that throughout the year there is a continuous, small flux of reactive N gases, dominated by $NH_3$, interspersed with short-term precipitation-induced large pulses of reactive N gases. In general, fluxes were higher in the spring than in the summer or fall (Figure 1.1). These observations are consistent with the mechanism that warmer temperatures and periodic rain events stimulate nutrient turnover during the spring growing season (Rundel and Gibson 1996, Fernandez et al. 2006).

Although seasonality was a significant factor in the characterization of N gas loss from soils, spatial variability associated with cover type did not influence NO or $NH_3$ flux estimates from dry soils in this study. This may be because under dry soil conditions, fluxes were not large enough for such patterns to be detectable or, alternatively, that plant cover does not play an important role in describing spatial patterns of NO or $NH_3$ emission in this system.

A rain event in October 2004 led to considerable increases in NO and $NH_3$ emissions (Figure 1.2). This is consistent with our understanding of the importance of pulse rain events in driving N dynamics and trace N gas loss in arid environments (Martin et al. 1998, Smart et al. 1999, Hartley and Schlesinger 2000, Austin et al. 2004). Following precipitation, there was spatial variation in N gas loss associated with cover type, with NO emissions being highest from soils under *L. tridentata*. Variation in soil nutrients between shrub and interspace soils have been well documented in arid ecosystems (Schlesinger et al. 1996) including the Mojave Desert (Romney et al. 1980, Titus et al. 2002). Shrubs such as *L. tridentata* promote high resource availability and more rapid N turnover and these patterns are presumed to drive the observed spatial variability in N gas loss. We did not see spatial patterns in $NH_3$ emission, nor did we see effects of cover types other than *Larrea* on NO emissions. However, time constraints imposed by our measurement system meant that

our post-rain event measurements were made over a 6-day period and day-to-day replication of a single measurement position was not possible. The largest differences across cover types in N gas emission, particularly $NH_3$ efflux, may have occurred immediately following the precipitation event.

In order to more fully elucidate the fine-scale mechanisms controlling nitrogen trace gas efflux from Mojave Desert soils we conducted a series of laboratory experiments. Multiple studies have shown that addition of water to dry soils can cause a large pulse of NO, due to the accumulation of N during dry periods and stimulation of microbial activity following soil wetting (eg. Anderson and Levine 1987; Davidson 1992; Hartley and Schlesinger 2000; Johansson et al. 1988; Rondon et al. 1993). Consistent with this literature, water addition during our laboratory experiments (Figure 1.4) resulted in a large NO pulse; however, this response was delayed relative to other studies that show NO fluxes peaking within hours of water addition (Davidson et al. 1991, Davidson et al. 1993, Martin et al. 2003, Barger et al. 2005, Neill et al. 2005). The delayed post-wetting NO pulse we observed in Mojave soils may be related to the immediate, large pulse of $NH_3$ volatilization that occurred in these soils (Figure 1.5). In experiments looking at interactions between $NH_3$ volatilization and nitrification, Praveen-Kumar and Aggarawal (1998) found that only one process, either nitrification or $NH_3$ volatilization occurred at a time. They proposed that toxic levels of $NH_4^+/NH_3$ inhibit nitrification especially in coarse textured alkaline soils, however, when conditions allow for nitrification, $NH_3$ volatilization is dramatically reduced, possibly due to rapid drawdown of $NH_4^+$ by nitrifiers. In our system, an initial pulse of $NH_4^+$ following soil wetting coupled with high alkalinity may have caused $NH_3$ volatilization at the exclusion of nitrification, thus delaying the NO pulse that typically coincides with soil wetting. Alternately, the delayed NO pulse could be the result of slow recovery of the nitrifier population following drought conditions.

We hypothesize that there are two potential sources of N for the large $NH_3$ pulse observed immediately after the addition of water to dry, desert soil. Volatilized $NH_3$ could come from either microbial biomass N released in response to changes in osmotic potential or from the dissolution of mineral N accumulated during the preceding dry period (Schlesinger and Peterjohn 1991, Davidson et al. 1993, Miller et al. 2004). It is likely that both are N sources; however the size of the $NH_3$ pulse and the fact that it is highest in interspace soils where nutrient accumulation is lowest (Vinton and Burke 1995, Titus et al. 2002), suggests that microbial biomass N could be a substantial component of the initial $NH_3$ flux. Changing osmotic conditions can result in the release of nutrients either by microbes lysing or pumping intercellular solutes into the soil solution to maintain osmotic balance (Kieft et al. 1987, Halverson et al. 2000). Experiments by Fierer and Schimel (2003) on the source of the post-rewetting $CO_2$ pulse suggest that the primary source of N in the soil solution following rewetting is intracellular solutes expelled by microbes. It is probable that the release of N happens faster than the microbial community can respond, thus in basic soils this, in combination with $NH_4^+$ accumulated during dry periods, appears to drive a large, transient pulse of $NH_3$ volatilization. In our system, this pulse was much lower in *Larrea* influenced soils suggesting that depending on the primary source of the $NH_3$, these microsites either have less accumulation of mineral N due to faster internal cycling or the microbial population is more resistant to changes in osmotic potential.

Following soil wetting, the composition and magnitude of N gas emissions from Mojave Desert soils was dictated largely by temperature and the nutrient status of the soil solution (Figures 1.4, 1.5). During periods of microbial activity, inorganic N is likely consumed in the system by three processes: (1) volatilization as $NH_3$, (2) immobilization by microbes or plants, or (3) utilization by nitrifying and denitrifying bacteria. The first and third processes produce $NH_3$ and NO, respectively, whereas the

second process retains N in the soil, reducing rates of N gas emission. The partitioning of N among these pathways is the result of competitive interactions among microorganisms, plants and chemical reactions, with the outcome being influenced by soil conditions, in our study temperature and nutrient availability. Our results suggest that in Mojave soils, temperature altered N gas loss by influencing rates of microbial processing of N, whereas the relative availability of labile C and N determined whether the dominant fate of N was immobilization or gaseous loss. When looking at the form in which N was lost to the atmosphere, timing as well as the abundance of inorganic N appeared to be an important determinant of NO versus $NH_3$ emission.

The importance of competitive interactions for inorganic N in determining the size and composition of trace N gas loss is reflected in the fact that fluxes of $NH_3$ and NO differed not only in the timing of the post-wetting pulse, but also in the response to changes in soil conditions. In dry soils, the magnitude of both NO and $NH_3$ emission was affected by temperature, however, the direction of this response was opposite for the two gas species. The observed increase in NO efflux with an increase in temperature is consistent with temperature regulating the metabolic activity of nitrifying and denitrifying bacteria, with low activity at low temperatures leading to minimal NO efflux (Skiba et al. 1993, Parton et al. 2001). The observed positive relationship between temperature and NO emissions, especially following soil wetting, is one that has been shown in other studies (Anderson and Levine 1987, Williams et al. 1988, Smart et al. 1999, Martin et al. 2003, Barger et al. 2005) although other responses to temperature have been reported (Johansson and Sanhueza 1988, Rondon et al. 1993, Serca et al. 1994, Aneja et al. 1995).

The reduction in $NH_3$ efflux we observed at higher temperatures in dry soils is more surprising, however, given the increase in NO production, it is likely that

increased microbial activity at high temperatures increased competition for $NH_4^+$, reducing the amount of substrate for $NH_3$ volatilization. In contrast to NO production, addition of water diminished the importance of temperature in determining rates of $NH_3$ volatilization. This response is likely the result of differences in timing between the stimulation of biological activity and peak $NH_3$ efflux. If the influence of temperature on $NH_3$ production is largely an indirect effect of changing competitive dynamics for $NH_4^+$, then the large post-wetting pulse of $NH_3$ likely occurs prior to the stimulation of microbial activity and is thus independent of direct temperature effects on the microbial community.

Nutrient availability, especially N availability, has been identified as an important determinant of N gas loss from soils. Numerous studies have shown that N additions stimulate NO production (eg. Cardenas et al. 1993; Hall and Matson 2003; Hartley and Schlesinger 2000; Johansson et al. 1988; Martin et al. 1998; Rondon et al. 1993; Sanhueza et al. 1990; Serca et al. 1994; Smart et al. 1999; Venterea et al. 2003). Excess inorganic N in the soil solution enhances NO loss either as a result of increased substrate availability for nitrifying and denitrifying bacteria (Davidson et al. 1993; Hartley and Schlesinger 2000; Mosier et al. 1998) or decreased consumption of NO by the microbial community (Stark et al. 2002). Our experiment added N in the form of $NO_3^-$, the primary substrate for denitrification as opposed to nitrification. It is possible the stimulation of NO loss by $NO_3^-$ addition is due to increased denitrification (Cardenas et al. 1993, Rondon et al. 1993); however most studies suggest nitrification is the primary source of NO (eg. Davidson et al. 1993; Hartley and Schlesinger 2000; Parton et al. 2001; Smart et al. 1999; Stark et al. 2002). It is likely the addition of $NO_3^-$ in our study reduced competition for N, either leaving more $NH_4^+$ available for nitrification or, as hypothesized by Stark et al. (2002), decreasing consumption of NO within the soil, increasing emission.

An alternative explanation for the observed high NO efflux following $NO_3^-$ addition is chemodenitrification. Under acidic conditions, $NO_2^-$ equilibrates with $H^+$ and the resulting $HNO_2$ can decompose under aqueous conditions to produce NO or can react with soil organic matter, also producing NO (Nelson 1982, Davidson 1992, Venterea and Rolston 2000). Abiotic production is less likely to be an important mechanism of NO production in Mojave Desert soils due to high pH; however, it has been suggested that even in highly alkaline soils, acidic microsites enable such reactions to occur (Nelson 1982). However, if the measured NO pulse was the result of direct chemical or microbial alteration of $NO_3^-$ then one would expect an immediate pulse following N addition instead of a 1 to 2 day delay in peak NO efflux.

Fewer studies have looked at the role of C availability in determining rates of NO emission; however, in our system C addition had a strong negative influence on post-wetting NO efflux. Studies that have investigated the role of labile C in determining rates of NO efflux have reported variable responses [no response to C addition (Bakwin et al. 1990, Smart et al. 1999), increased fluxes (Slemr and Seiler 1991) and flux suppression (Matson et al. 1996)]. Increased fluxes of NO after C addition have been attributed to increased denitrification (Slemr and Seiler 1991) whereas decreases are thought to be the result of increased microbial immobilization of N (Matson et al. 1996). Increased microbial immobilization of N following labile C addition in Mojave Desert soils supports the conclusion of Schaeffer et al (2003) that microbial activity in Mojave soil crusts is limited by the availability of labile C. Additionally, labile C has been shown to stimulate microbial immobilization of N in other arid and semi-arid ecosystems (Gallardo and Schlesinger 1992, 1995, Stark et al. 2002, Schaeffer et al. 2003, Schaeffer and Evans 2005). In the present study, the influence of carbon addition was much stronger in soils from interspaces between shrubs. This is likely driven by higher soil organic matter contents beneath *Larrea*

(Schaeffer et al. 2003, Ewing et al. 2007) making microbial activity in these soils less C limited and therefore less sensitive to additional C.

In general, $NH_3$ volatilization was less responsive than NO production to changes in nutrient availability. Nitrate addition did not substantially alter the initial $NH_3$ pulse following soil wetting, however, in interspace soils, $NH_3$ emissions remained elevated for several days suggesting that this processes is sensitive to changes in $NO_3^-$ availability. This prolonged period of $NH_3$ volatilization is likely driven by reduced competition for N leading to higher $NH_4^+$ availability (*sensu* Schlesinger and Peterjohn 1991). The fact that this response did not occur in *Larrea* influenced soils suggests higher soil C content enabled microbial immobilization of the added $NO_3^-$ (Zaady et al. 1996, Schaeffer et al. 2003). As with $NO_3^-$ addition, the initial pulse of $NH_3$ following soil wetting was insensitive to changes in labile C, however, C addition did alter the rate at which fluxes returned to baseline values. Increased C availability accelerated the decline in $NH_3$ efflux, presumably due to the same mechanism hypothesized for the suppression of NO emission. In addition to decreasing nitrification, increased N immobilization would draw down the pool of $NH_4^+$ available for volatilization, thus reducing $NH_3$ efflux.

The observation that the initial pulse of $NH_3$ following water addition is insensitive to temperature, and $NO_3^-$ and C addition suggests that following precipitation a portion of the N released into the soil solution is lost to the atmosphere before microbial activity is stimulated. During this period, $NH_3$ volatilization proceeds uninhibited by competition for $NH_4^+$ and therefore is insensitive to factors such as temperature and labile C that alter rates of N immobilization and nitrification. Subsequently, microbial activity is up-regulated in response to increased water availability and rates of $NH_3$ volatilization, although still elevated over baseline levels, are constrained by microbial and presumably plant uptake of $NH_4^+$.

The combination of laboratory and field measurements presented in this study indicate that N gas production in the form of NO and $NH_3$ is an important component of Mojave Desert N dynamics, with $NH_3$ production being a significant loss term. Similar to studies addressing controls over NO production, we have found that water addition exerts a strong control over rates of $NH_3$ emission. Although temperature and nutrient availability are important constraints on $NH_3$ efflux, unlike NO production the sensitivity of $NH_3$ emissions to these factors is time dependent, with initial pulses of $NH_3$ after water addition being relatively insensitive to alterations in soil conditions. Moreover, the presence of high rates of $NH_3$ volatilization appears to alter NO responses to water addition, delaying the post-wetting NO pulse frequently observed in other systems by several days. These results suggest both that $NH_3$ production needs to be included in estimates of N dynamics in ecosystems with highly alkaline soils and that in these systems $NH_3$ volatilization needs to be considered when studying controls over other processes, such as NO production, that are sensitive to concentrations of $NH_4^+$.

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CHAPTER 2

# ABIOTIC GAS FORMATION DRIVES NITROGEN LOSS FROM A DESERT ECOSYSTEM[1]


## Abstract

In arid environments such as deserts, nitrogen (N) is often the most limiting nutrient for biological activity. The majority of the ecosystem N-flux is typically thought to be driven by production and loss of reactive N species by microorganisms in the soil. We found that high soil surface temperatures (>50˚C), driven by solar radiation, are the primary cause of N loss in Mojave Desert Soils. This abiotic pathway not only enables the balancing of arid ecosystem N budgets, but also changes our view of global N cycling and the predicted impact of climate change and increased temperatures on N bioavailability.


## Report

After water, nitrogen (N) availability is the primary constraint to biological activity in many arid ecosystems (Whitford 2002). Despite the presence of large pools of soil N, arid regions such as deserts, dry shrublands, and savannahs often lack bioavailable forms of N (West and Klemmedson 1978, Billings et al. 2004). Inputs and losses of biologically available N therefore directly impact ecosystem productivity. Gaseous emissions from soil are thought to be the primary form of N export in arid lands, and are estimated to be as much as 1-3 kg N $ha^{-1}$ $y^{-1}$ in arid regions of North America and Africa (Peterjohn and Schlesinger 1990, Feig et al.

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2008). To date, annual estimates of N loss from deserts have been calculated based on measurements of inputs and storage and have included little direct characterization of N loss dynamics. It has been assumed that differences between N inputs and storage can be attributed to microbial activities which produce trace N gases at the soil surface, with emissions being driven by nitrification and denitrification during the growing season (Firestone and Davidson 1989). Recent studies have shown, however, that N loss patterns are inconsistent with biological mechanisms of N gas production. For example, of the ~ 1 kg N $ha^{-1}$ $y^{-1}$ estimated N loss in the northern Mojave Desert in the form of reactive N gases (i.e., nitrogen oxides and $NH_3$), approximately 75% occurs in the summer under conditions hostile to biological activity (McCalley and Sparks 2008). Abiotic formation of N gases may therefore be the dominant form of N export in the Mojave and is likely to drive N loss in most arid ecosystems. Identification and quantification of this flux will potentially account for the N imbalance in arid regions (Rundel and Gibson 1996).

We used field and laboratory approaches to monitor production of reactive N from Mojave Desert soils and to describe the underlying mechanisms. In this context, we defined reactive nitrogenous gases as nitrogen oxides ($NO_y$; all forms of oxidized gaseous N) and $NH_3$. We excluded less reactive chemical species (e.g., $N_2$ and $N_2O$) as they have previously been measured or estimated and shown to be a minor component of N loss in this and other arid regions (Billings et al. 2002, Johnson et al. 2007). Summer in the Mojave Desert yields extreme diurnal patterns in light and soil temperature that allowed us to test abiotic formation of reactive N. We monitored total reactive N fluxes, segregated as NO, other forms of $NO_y$ and $NH_3$, starting before dawn and continuing until after dark in both naturally dry soils and 24 hours after an artificial 25 mm rain event. Measurements were replicated across the range of soil heterogeneity typical of deserts (Schlesinger et al. 1996) and included both plant

interspaces and soils influenced by the dominant shrub *Larrea tridentata*. To further explore the effect of solar radiation on abiotic formation of reactive N, radiation shields were used in the field to induce short-term flux responses to the complete removal of light and reductions in soil temperature associated with solar radiation. These field manipulations of solar radiation, however, did not allow for the separation of the direct (light) and indirect (temperature) effects of solar radiation on the chemical formation of reactive N gases. To identify the individual effect of temperature on reactive N gas emissions, we manipulated surface temperatures of intact soil profiles from 15 – 75 ºC and measured production of nitrogen oxides and ammonia as well as soil respiration. Measurements were made on soils collected from interspaces covered in biological soil crust and from beneath *L. tridentata* and were either dry or watered to field capacity and allowed to dry for 60 hrs.

In the field, we attributed production of reactive N from dry soils to abiotic processes and, additionally, fluxes from wet soils during midday peaks in radiation and soil temperature [midday ground temperatures during measurements were > 65 ˚C and can exceed 90 ºC in the Mojave Desert (Rosentreter and Belnap 2001)] were also attributed to non-biological sources. Diurnal measurements showed strong daily patterns of reactive N gas efflux, with emissions peaking at midday when soil radiation approaches 1000 W $m^{-2}$ and surface soil temperatures exceed 60 º (Figure 2.1). Maximum fluxes from dry soils were 5.5 ng N $m^{-2}$ $s^{-1}$. This value is similar to flux estimates (consisting only of NO) attributed to biological nitrification reported in tropical woodlands, that are thought to have some of the highest rates of biological reactive N gas production (Davidson and Kingerlee 1997). A diurnal pattern was also clearly present in recently wetted soils (Figure 2.1). However, the response was several orders of magnitude larger than that in dry soils with fluxes reaching 160 ng N $m^{-2}$ $s^{-1}$, a rate comparable to some of the largest pulses of biological NO reported for

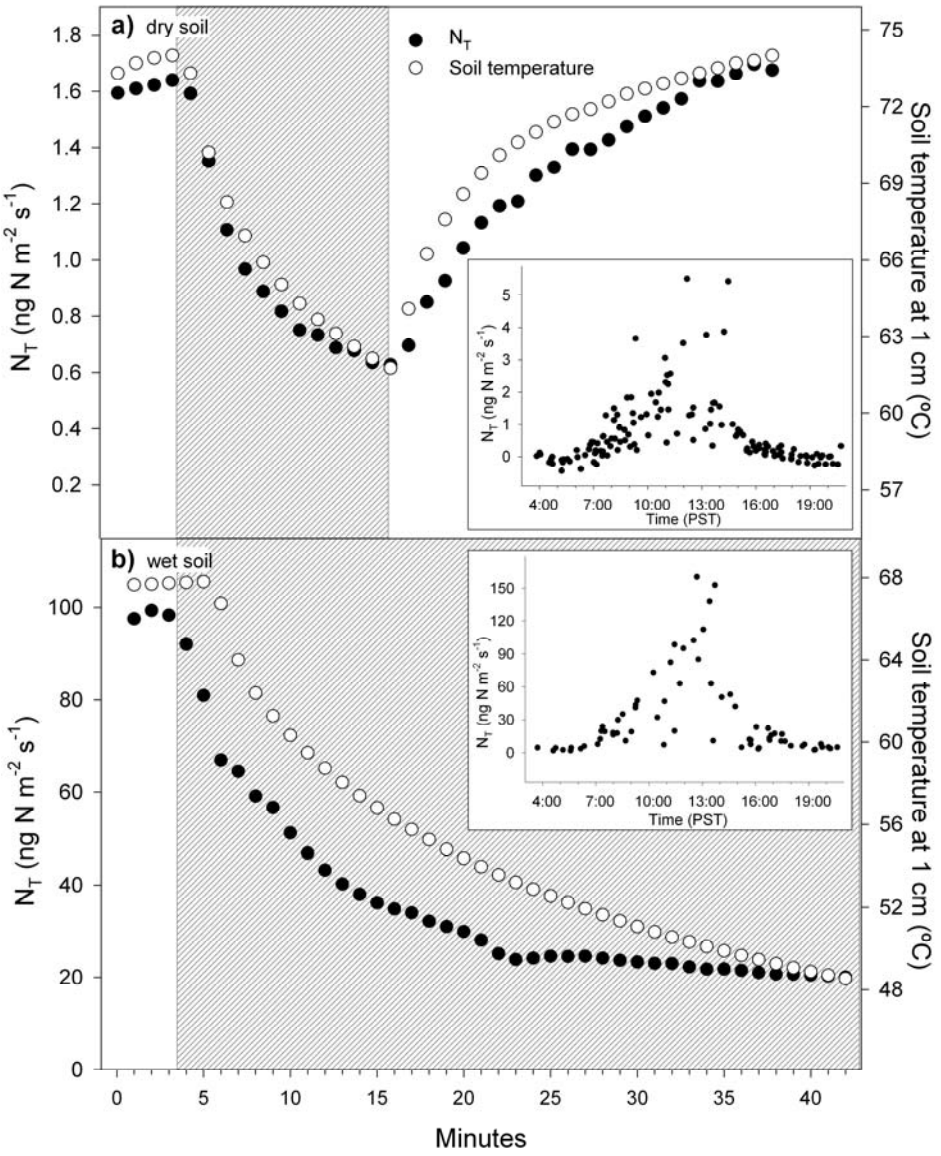


**Figure 2.1** Soil measurements of the response of total reactive nitrogen ($N_T$) gas emissions to changes in solar radiation from **(a)** dry soil and **(b)** 24 hrs after an artificial 25 mm rain event. The main panels show the responses of N gas fluxes and soil temperature in plant interspaces during the removal of all incoming radiation; shaded areas indicate periods when all incoming solar radiation was blocked using a radiation shield. Shading responses were measured at midday, between 12 and 2 pm. Each inset shows the diurnal pattern of reactive N gas emissions during the summer across a heterogeneous landscape under dry and wet soil conditions, respectively. Each data point is an individual measurement and the diurnal pattern includes data points collected on multiple days during two successive summers (2007 & 2008). The composition of the flux differed between the two treatment conditions. Fluxes from dry soils were 19% NO, 55% other forms of $NO_y$, and 26% $NH_3$. In contrast, emissions from wetted soils were 62% NO, 25% other forms of $NO_y$, and 13% $NH_3$.

natural systems (Davidson et al. 1993). The continued presence of a diurnal flux pattern in wet soils contrasts with other studies of post-rain measurements of N gas efflux (Davidson et al. 1991, Barger et al. 2005) where fluxes rapidly decline following an initial pulse and emphasizes the role of abiotic processes in describing N gas loss patterns from Mojave Desert soils. Light removal experiments conducted during the midday peak in reactive N gas efflux on interspace soils yielded conclusive evidence for the importance of solar radiation in driving N gas loss from desert soils. There was an immediate decrease in both reactive N gas emissions and soil temperature at 1 cm in response to changing light conditions and the removal of light resulted in significant reductions in total reactive N gas efflux from both wet and dry soils ($p<0.05$) (Figure 2.1). The same response was recorded for soils beneath *L. tridentata* (Table 2.1). The temporal offset between the response in N gas emission and temperature observed in wet soils is likely due to the slight delay in temperature propagation to the depth of the temperature measurement. The immediacy of this response makes it unlikely that flux reductions are driven by changes in soil N availability associated with autotrophic N fixation; instead the response appears to be closely linked to light dependent changes in surface soil temperature.

**Table 2.1** Summary of light and dark measurements of total reactive N gas fluxes ($N_T$) and soil temperature at 1 cm depth (error = ± SE, n = 8).

| | **$N_T$ Flux (ng N $m^{-2}$ $s^{-1}$)** | | **Soil Temperature (°C)** | |
|---|---|---|---|---|
| **Treatment** | Light | Dark | Light | Dark |
| Interspace, pre-irrigation | 1.9 (0.3) | 0.7 (0.1) | 68.2 (1.9) | 59.2 (0.9) |
| *L. tridentata*, pre-irrigation | 3.4 (0.6) | 1 (0.1) | 70.7 (2.9) | 57.2 (0.8) |
| Interspace, post-irrigation | 78.8 (10.5) | 18.5 (3.0) | 64.7 (2.2) | 44.6 (2.4) |
| *L. tridentata*, post-irrigation | 118 (16.4) | 39.7 (9.4) | 63.8 (1.1) | 48 (1.2) |

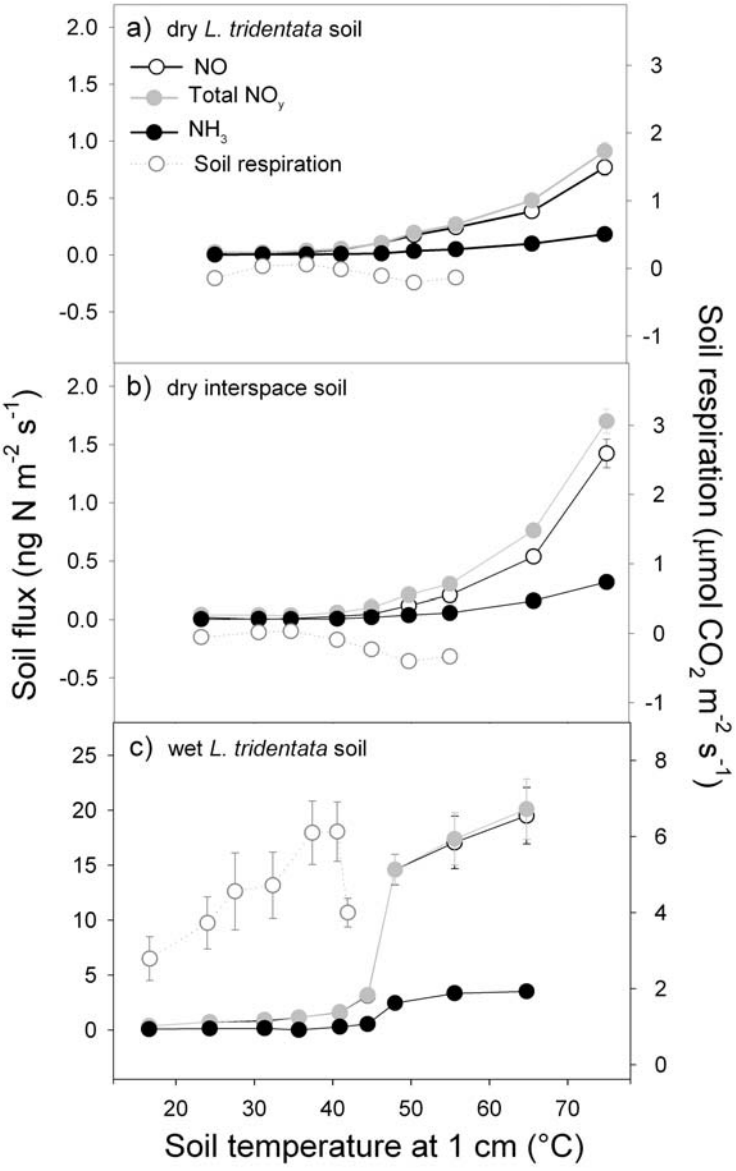


**Figure 2.2** Laboratory measurements of the response of reactive N gas emissions and soil respiration to changes in soil temperature in **(a)** dry soil from beneath *L. tridentata*, **(b)** dry soil from plant interspaces, and **(c)** wetted soil from beneath *L.tridentata*.

The correlation between surface soil temperature and reactive N gas efflux was further supported by the results of laboratory manipulations where temperature was varied under constant, low-level light conditions (350 μE) (Figure 2.2). In dry soils, reactive N gas fluxes increased ($p < 0.0001$) with surface soil temperature for both cover types (Figure 2.2), with losses increasing from 0.05 to 2 ng N $m^{-2}$ $s^{-1}$ over a

temperature range of 20 – 70 ˚C. Soil temperatures of 40-50 ºC were an important threshold for this response, lower temperatures had little effect on fluxes, and higher temperatures had a strong positive effect on fluxes. No detectable soil respiration occurred in dry soils, indicating that the N gas production is driven exclusively by abiotic mechanisms. Wet soils showed a similar response to increasing temperature ($p < 0.0001$), however, fluxes were an order of magnitude higher (Figure 2.2). In wet soils, respiration showed a positive relationship with temperature up to 40 ºC, abruptly declined as temperatures exceeded 40 ºC, and was then unmeasurable by our system at temperatures > 50 ˚C. Differential responses of soil respiration and reactive N gas production to changing soil temperature support the hypothesis that N gas emissions are driven by non-biological processes. Respiration was not assessed at the highest temperatures (> 50 ˚C) because the $CO_2$ monitoring equipment would not operate at these temperatures, but multiple studies have shown that microbial processes that produce reactive N are inhibited at temperatures exceeding 40°C (Sierra and Marban 2000, Passianoto et al. 2004, Luxhoi et al. 2008). Thus biological activity is very unlikely to significantly contribute to the flux of reactive N during these periods of high reactive N gas loss.

Our results show that abiotic reactions are a key component of N loss from desert soils, both under dry conditions and during post-wetting periods. Not only is there a continuous chemical loss of N from dry soils, but following soil wetting there is a substantial increase in production of reactive N gas that cannot be attributed entirely to biological activity. This increased loss rate is likely a combined effect of higher concentrations of biologically produced substrate and a faster rate of reactions when substrates more readily enter solution. Such high rates of abiotic N gas loss from both wet and dry soils suggests that traditional measurement approaches that avoid dry soil and summertime conditions underestimate total N gas loss from desert soils and

may misrepresent patterns and sources of these gases. Abiotic decomposition of $HNO_2$ to NO (chemodenitrification) can drive N gas loss in soils. However, it occurs exclusively in wet, acidic soil microsites (Venterea and Rolston 2000) and is therefore unlikely to explain the abiotic N gas production observed in the highly alkaline soils used in this study. Therefore, the observation reported here of abiotic nitrogen gas production from desert soils identifies a gap in our understanding. The mechanism is likely high temperature oxidation of organic and/or inorganic nitrogen. However, these processes have only been shown to occur at higher temperatures (Phillips 1947, Stern 2001) and now must be considered to potentially occur at lower temperatures.

In addition to dominating arid-land N export, soil emissions of N gases yield reactive nitrogenous chemical species (e.g., NO, $NO_2$ and $NH_3$) with relatively short atmospheric lifetimes that drive several aspects of regional air quality including ozone chemistry and aerosol formation (Jacob 1999). In contrast to less reactive N gases such as $N_2O$ and $N_2$, that are stable in the troposphere, the reactivity of these chemical species often means that local sources, including soil fluxes, drive atmospheric chemistry on a regional scale (Honrath et al. 2000). This is especially true in remote regions. For example, in Antarctica and other isolated snow covered areas, photochemical reactions in snow yield N gases that impact the oxidizing capacity of the troposphere (Grannas et al. 2007). Such fluxes of reactive N peak around 0.3 ng N $m^{-2}$ $s^{-1}$ (Honrath et al. 2002), less than 20 % of midday emissions into the atmosphere above the Mojave Desert. Given the magnitude of desert fluxes relative to those found to be important in polar regions, it follows that the abiotic reactions identified in this study can play an important role in atmospheric processes above remote arid sites.

The high proportion of reactive N gas efflux associated with abiotic sources suggests that, similar to carbon released during photodegradation of litter (Austin and Vivanco 2006), N in arid environments can bypass biotic pools by returning directly to

the atmosphere via abiotic pathways. This decoupling of nutrient dynamics from biological processes in water limited ecosystems means we must consider how arid environments may respond to global change. Carbon dynamics in water-limited ecosystems may be most sensitive to global change factors that alter the composition and intensity of radiation reaching the earth's surface (Davidson et al. 1991). Our study not only identifies N cycling as being equally sensitive to solar radiation as carbon, but also highly temperature dependent. Ultimately, rates of N export from arid ecosystems will be determined by summer surface soil temperatures and the frequency of summer precipitation events, both of which are predicted to change under most scenarios of future global climate (Solomon et al. 2007). Interestingly, the conditions that promote abiotic N gas loss from desert soils also inhibits N fixation (Belnap 2001), the dominant N input to arid regions. Future environmental shifts will therefore likely disrupt natural N dynamics by unbalancing rates of N inputs and loses, gradually reinforcing N limitations in arid environments.

**Supporting Material - Methods**

*Study Site*

The field component of this study was conducted at the Mojave Global Change Facility and the Nevada Desert FACE Facility located in Nye County, Nevada (36°49'N, 115°55'W), 90 km northwest of Las Vegas, NV USA at an elevation of 970 m. The site lies within the Nevada Test Site, administered by the US Department of Energy and has been protected from recreation and grazing disturbances for approximately 50 years (Jordan et al. 1999). Mean annual rainfall is 140 mm and precipitation occurs primarily as winter storms and as short, localized summer events. Temperatures range from winter minima of -10°C to summer temperatures > 47°C. The site is a *Larrea tridentata – Ambrosia dumosa* plant community and has intact

biological soil crusts covering ~20% of the soil surface (Titus et al. 2002). Soils are Aridisols derived from calcareous alluvium with a loamy sand texture (89% sand, 6% silt and 5% clay). Subsoils lack a caliche layer, resulting in well-drained soils. Soil pH, measured in water, at the site ranges from 9-11 and soils are spatially heterogeneous in nutrients, texture and infiltration (Romney et al. 1980).

*Reactive N Gas Flux Measurements*

Nitrogen gas fluxes (NO, $NO_y$, and $NH_3$) were measured using selective thermal and chemical decomposition converters to reduce or oxidize all reactive nitrogen trace gases (e.g., oxidized forms and ammonia) to NO. During measurement, a sealed, top with two ports was placed over the soil collar, the cuvette material used in this study allowed the transmission of wavelengths >400 nm meaning we did not record emissions driven by shorter wavelengths. One port remained open to the atmosphere, which minimizes induced pressure differences associated with closed chamber based measurement techniques. To make a measurement, outside air was passed, at 1 L $min^{-1}$, either directly to the measurement system to quantify background air concentrations, or through the soil collar and then to the measurement system to quantify soil emissions. The measurement system consisted of two conversion cells that reduce $NO_y$ (total oxidized N) and total reactive N ($NO_y$ + $NH_3$) to NO, respectively, and a chemiluminescence NO detector (Thermal Electron Corporation 42*i*-TL). Each converter can be isolated by Teflon valves and independent measurements can be made for NO (no conversion), $NO_y$ ($NO_y$ converter only), and total reactive N ($NH_3$ + $NO_y$ conversion). Fluxes were calculated based on steady-state concentrations using the equation C * q/A where C is concentration (nmol $L^{-1}$), q is the flow rate (L $s^{-1}$) and A is area ($m^2$) of the soil surface. Concentrations used for calculation were soil chamber minus air concentrations for any particular

measurements. Ammonia fluxes were calculated by subtracting the total $NO_y$ value from the total reactive N value. Measurements of NO, $NO_y$ and $NH_3$ were made sequentially and total measurement time averaged 20-30 min.

The $NH_3$ conversion cell consists of a 30 cm length of nickel-chromium alloy tubing (INCONEL 600) passed through a mini tube furnace (Lindburg/Blue Mini-Mite Tube Furnace) heated to 825 ˚C. Laboratory calibrations of the converter have shown 86% conversion efficiency for $NH_3$ with no influence on NO concentration. The $NO_y$ converter is a heated glass catalytic converter that contains a 60-cm piece of ¼" gold tube heated to 300°C. A small flow of $H_2$ (30 mL $min^{-1}$) is introduced just prior to the heated region to facilitate the reduction of oxidized N to NO. Laboratory calibration tests have shown a 100% conversion of $NO_2$ and HONO and conversion efficiencies between 78 – 99% for other components of $NO_y$ (i.e., peroxyacetyl nitrate, alkyl nitrate, $HNO_3$ and other forms of $NO_y$ usually formed in the atmosphere).

After conversion (or directly in the case of the NO only measurement), air is passed through an NO analyzer (Thermo Electron Corporation, Model 42*i* TL). This instrument detects light from the chemiluminescence reaction between NO and $O_3$:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\upsilon$$

The analyzer avoids interferences (a common problem with many NO analyzers) using a pre-reaction chamber where $O_3$ is used to consume NO before entering the reaction chamber. Because the rate of reaction with NO is very fast and the reaction with most interference compounds is relatively slower, two sequential runs (the first utilizing the pre-reaction cell and second going directly to the sample cell without pre-reaction) allows for the quantification of NO independent of all interferences and gives instrument a detection limit of 50 pptv. The instrument was calibrated by sequential dilution of an NO standard (Scott Specialty Gases, Irvine, CA) daily.

*Diurnal Measurements*

Instantaneous flux measurements of NO, $NO_y$ and $NH_3$ were made in July 2007 starting before dawn and continuing until after dark. Measurements were continually made on 4 soil collars per day, resulting in individual collars being visited at approximately 2 hour intervals. Daily flux patterns were quantified for a total of 16 collars in dry soils (~6% volumetric water content) and 8 collars 24 hrs after a 25 mm artificial rain event. Soil collars were 25.5 cm diameter, 15 cm tall, and were installed approximately 7.5 cm into the soil profile in June 2004. Collars were installed evenly across the following cover types: under the evergreen shrub *Larrea tridentata* (creosote bush), under the $C_4$ bunchgrass *Pleuraphis rigida* (big gaelleta), soil interspace with visible biological soil crust, and soil interspace with no visible crust. Visibility of the biological soil crust was determined qualitatively by the presence or absence of lichen and moss. Additional diurnal measurements were made in July 2008 using 16 collars, 8 each in interspace and *L. tridentata* soils. In 2008, measurements were made between 8 am and 6 pm and were made in naturally dry soils (~6% volumetric water content) and 24 hrs after a 25 mm artificial rain event.

*Light Removal Experiment*

In July 2008, a radiation shield made from opaque, reflective material was used to monitor the direct and indirect effects of solar radiation on total reactive N gas efflux ($N_T$) during peak periods of solar radiation (11 am - 3 pm). Responses were measured in the same interspace and *L. tridentata* soils used in the 2008 diurnal measurements and were replicated before and 24 hrs after a 25 mm artificial rain event. During the experiment $N_T$ and surface soil temperature (top 1 cm) were measured every 10 seconds and the radiation shield was added and then removed after $N_T$ reached stability. The effect of blocking solar radiation was determined by

comparing the stable light and dark $N_T$ emissions. All interspace and *L. tridentata* soils showed the same response pattern to blocking solar radiation, therefore only one individual response is shown in Figure 2.1, the remaining responses are summarized in Table 2.1.

*Laboratory Soil Temperature Experiment*

Soils for the laboratory experiment were collected in January 2007 adjacent to the site of field measurements during a time period when microbial populations are naturally dormant due to low soil temperature (± 5°C) and moisture (< 5% volumetric water content). Intact soil profiles, 15.2 cm diameter and 8 cm deep, were collected from interspace soils and from beneath *L. tridentata* (n = 5) and transported to Cornell University. Low moisture conditions during soil collection and transport enabled the maintenance of dormancy in microbial populations. During measurements, soil profiles were incubated in a growth chamber (Conviron, CMP 3244), and soil temperature at 1 and 5 cm were measured every 10 seconds (type T thermocouple, Campbell Scientific CR23X datalogger). Measurements of reactive N gas emissions and soil respiration were made on each collar after bring incubated for 24 hrs at 10, 20, 25, 30, 35, 40, and 45 ºC. Soil temperatures were raised an additional 10 and 20 °C by adding an infra-red heat lamp to the growth chamber. Soil respiration was measured using an LI-6400 infrared gas analyzer (LiCor Biosciences) with the cuvette modified to fit the experimental collars. Respiration measurements were not made at the two highest temperatures due to the system not being designed to withstand these extreme temperatures. Collars were given a 12 hr photoperiod with a daytime light intensity of 350 μE. Measurements were made on naturally dry soils and on soils wet to field capacity and allowed to dry for 60 hrs. Moisture content was maintained in the wet treatment by daily additions of water to maintain a constant weight.

*Statistical Analysis*

We used a paired t-test (PROC TTEST, SAS 9.1) to determine the effects of light removal on total reactive N gas efflux from wet and dry soils. A repeated measures ANOVA (PROC MIXED, SAS 9.1) was used to determine the effect of temperature treatments on NO, $NO_y$ and $NH_3$ fluxes as well as soil respiration in the laboratory experiment. All analyses were performed using SAS statistical software (Cary, NC). Statistical significance was determined at $\alpha = 0.05$. Errors are presented as ±1 SE.

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CHAPTER 3

# THE EFFECT OF LONG-TERM EXPOSURE TO ELEVATED $CO_2$ ON NITROGEN GAS EMISSIONS FROM MOJAVE DESERT SOILS


## Abstract

In arid regions, emissions of N gases play an important role in long-term soil fertility as well as regional atmospheric chemistry, making alterations in N gas emissions an important aspect of ecosystem response to climate change. Studies at the Nevada Desert FACE Facility (NDFF) have suggested that rising atmospheric $CO_2$ concentrations impact ecosystems N dynamics in the Mojave Desert and our objective was to identify whether those responses translate into changes in soil emissions of trace N gases. We measured soil fluxes of reactive N gases (NO, $NO_y$, $NH_3$) and $N_2O$ in plots receiving long-term fumigation with ambient and elevated (550 ppm) $CO_2$ concentrations. There were significant reductions in reactive N gas efflux under elevated $CO_2$, with the strongest responses occurring in the islands of fertility created by the dominant shrub *Larrea tridentata*. Changes in total N gas emissions were driven by reductions in NO and $NH_3$, with smaller changes in $NO_y$ efflux and little to no production of $N_2O$ in any soils. Decreases in N gas fluxes under elevated $CO_2$ were most pronounced when temperatures were moderate and soil moisture high, with reductions of 3-5 ng N $m^{-2}$ $s^{-1}$ during the spring and fall, compared to ~ 0.2 ng N $m^{-2}$ $s^{-1}$ in winter. Nitrogen gas fluxes were insensitive to elevated $CO_2$ both when soil moisture was low and temperatures were high. Reductions in N gas emissions under elevated $CO_2$ reflect changes in microbial demand for N including decreased N mineralization and nitrification and increased N immobilization. This response of N gas efflux to elevated $CO_2$ in the spring and fall suggests that in deserts, elevated $CO_2$ promotes ecosystem retention of labile N during periods of peak biological demand.

Concomitantly, exposure to elevated $CO_2$ also alters inputs of new reactive gases into the atmosphere, potentially impacting local atmospheric processes in otherwise pristine and remote arid regions.

**Introduction**

In arid ecosystems, gaseous nitrogen (N) fluxes are often a substantial proportion of annual N loss, directly affecting its long-term bioavailability (Peterjohn and Schlesinger 1990, McCalley and Sparks 2008). Therefore, an essential part of understanding the impact of global climate change on arid regions is evaluating how the magnitude and composition of N emissions will respond to future environmental conditions, including rising atmospheric $CO_2$ concentrations. This is of particular importance given the role of N availability in determining growth responses to increased $CO_2$ (Hungate et al. 2003, Reich et al. 2006). In arid regions, responses to elevated $CO_2$ are highly correlated to water availability, with the strongest increases in productivity under elevated $CO_2$ occurring during periods of high precipitation (Smith et al. 2000, Naumburg et al. 2003). It is likely that during these periods when strong $CO_2$ effects are physiologically possible, bioavailability of soil N acts as a secondary constraint on the utilization of higher $CO_2$ concentrations. This means that a long-term change in the bioavailability of N under elevated $CO_2$ is likely to be an important variable in the response of desert communities to rising atmospheric $CO_2$.

Gaseous N species emitted from soil also directly impact key atmospheric processes associated with climate and air quality. Nitrogen gases produced in desert soils include nitric oxide (NO), a group of other reactive nitrogen oxides including HONO, $HNO_3$, $NO_2$ and organic oxides, which are categorized as $NO_y$, ammonia ($NH_3$) and nitrous oxide ($N_2O$) all of which participate in the chemistry governing climate. Nitrogen oxides are necessary precursors driving ozone formation in the

troposphere, a strong greenhouse gas and detrimental pollutant (Crutzen 1979, Solomon et al. 2007), nitrous oxide is a potent greenhouse gas with 200x the warming capacity of $CO_2$, and $NH_3$ participates in atmospheric aerosol production and cloud formation, influencing the attenuation of radiation and, therefore, the cooling of the Earth's surface (Solomon et al. 2007). Therefore, changes in both the magnitude and composition of soil nitrogen trace gas fluxes have the potential to influence important atmospheric processes, with the nature of this response being dependent on which gas species have a strong reaction to rising $CO_2$ concentrations.

The production of nitrogen gases in soils occurs through several different pathways, each of which has the potential to respond differently to changes in atmospheric $CO_2$ (Figure 3.1). Nitric oxide and $N_2O$ efflux are products of the microbe-mediated processes of nitrification and denitrification (Firestone and Davidson 1989), with NO production in arid ecosystems resulting primarily from nitrification (Smart et al. 1999, Hartley and Schlesinger 2000). Ammonia emissions are the result of chemical transformations of mineralized $NH_4^+$ under the basic soil conditions prevalent in arid regions (Schlesinger and Peterjohn 1991). In desert soils, nitrogen oxides and $NH_3$ may also be produced at high surface soil temperatures yielding substantial summertime losses, especially following precipitation (McCalley and Sparks 2009). Gaseous N losses are sensitive to (1) release of labile N from N fixation and decomposition of plant material (2) mineralization of organic N to $NH_4^+$ (3) nitrification and (4) uptake of $NH_4^+$ and $NO_3^-$ by plants and microbes (Fig. 1). Pool dynamics of soil $NH_4^+$ are a key driver of gaseous N losses; soil solution $NH_4^+$ concentrations which reflect the balance of mineralization and uptake of labile N are often a primary control over both $NH_3$ volatilization and the production of NO through nitrification (Schlesinger and Peterjohn 1991, Parton et al. 2001). In arid ecosystems studies have found that soil fluxes of N gases are sensitive to both direct additions of

inorganic N which change resource availability for $NH_3$ volatilization and nitrification, but also additions of labile C that increase microbial demand for and uptake of N (Schaeffer et al. 2003, McCalley and Sparks 2008). Nitrogen gas fluxes are therefore responsive to changes in both labile pools of soil C and N and can be indicators of alterations in microbial utilization of N as well as the turnover rate and availability of labile N.

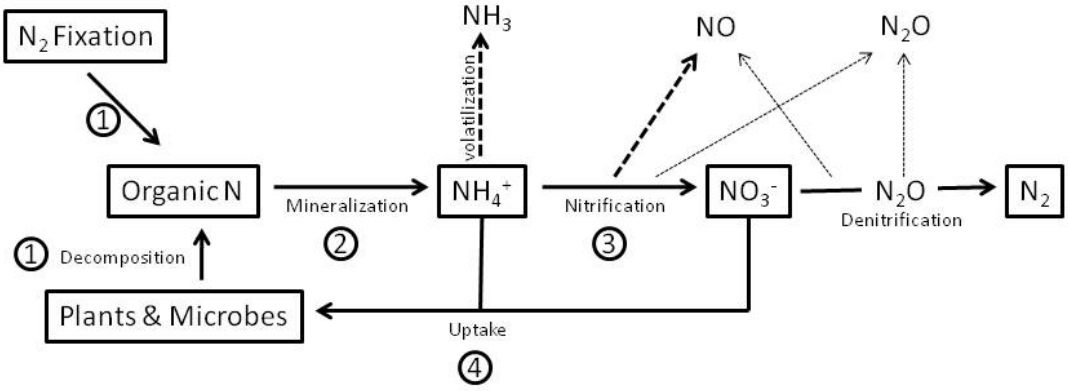


**Figure 3.1** Primary pathways for trace N gas production in arid ecosystems, dominant and minor pathways are indicated with dark and light lines respectively. Soil emissions are hypothesized to be sensitive to changes in (1) processes generating labile N, (2) mineralization of organic N to $NH_4^+$ (3) nitrification and (4) uptake of $NH_4^+$ and $NO_3^-$.

Elevated $CO_2$ has the potential to alter gaseous N losses through changes in the instantaneous availability of soil resources arising from shifts in inputs of labile N or microbial metabolism of soil N. General patterns in how belowground processes respond to elevated $CO_2$ including increased respiration, N immobilization and microbial N demand all suggest that elevated $CO_2$ has the potential reduce gaseous losses due to increased retention of N by the microbial community (Zak et al. 2000, de Graaff et al. 2006). However, responses of specific variables that yield N gas emissions such as nitrification, denitrification and mineralization show a highly variable response and have been found to increase, decrease, or not change under elevated $CO_2$ (Zak et al. 2000, de Graaff et al. 2006). Few studies that address the impacts of elevated $CO_2$ on soil N dynamics quantify changes in gaseous N emissions;

however, we propose that responses of N gas fluxes provide a metric for understanding ecosystem changes under elevated $CO_2$. Increases in N gas fluxes under elevated $CO_2$ reflect changes in soil nutrient cycling that increase availability of labile N, such as increases in N fixation and litter inputs or decreases in microbial uptake of inorganic N. Alternatively decreases in N gas emissions are indicative of reduced availability of labile N resulting from decreased inputs and/or increased uptake by plant and microbial communities.

At the Nevada Desert FACE Facility (NDFF), where an intact Mojave Desert ecosystem has been exposed to elevated $CO_2$ concentrations of 550 ppm since 1997, multiple studies have documented alterations in the N cycle under elevated $CO_2$ (Billings et al. 2002a, Billings et al. 2002b, Billings et al. 2004, Jin and Evans 2007, Schaeffer et al. 2007). The aim of this study was to identify whether ecosystem responses to elevated $CO_2$ translate into changes in N gas production and to use that information to further our understanding of the effects of elevated $CO_2$ on soil N cycling in arid ecosystems. Deserts are characterized by high spatial and temporal variability in microbial activity and soil resources therefore we sought to incorporate this natural range of environmental conditions into our understanding of the effects of elevated $CO_2$ on gaseous N loss. We quantified N emissions not only when high soil moisture enables biological activity, but also during dormant periods when abiotic processes drive N gas production. We hypothesized that during periods of high biological activity, changes in microbial activity under elevated $CO_2$ would alter in trace N gas fluxes, reflecting changes in the availability of labile N. However, during times of the year when abiotic processes dominate trace N gas efflux and physical environmental conditions are the primary drivers of N gas fluxes, emissions are hypothesized to be less sensitive to changes in atmospheric $CO_2$. Within this seasonal variation in the response of N gas production to elevated $CO_2$, we predicted that

spatial patterns in soil resources and plant responses to elevated $CO_2$ should be evident, with changes in N gas emissions under elevated $CO_2$ being larger in the 'islands of fertility' created by the dominant shrub *Larrea tridentata* (Schlesinger et al. 1996, Titus et al. 2002).

## Methods

*Study Site*

Measurements were conducted at the Nevada Desert FACE Facility located in Nye County, Nevada (36°49'N, 115°55'W), 90 km northwest of Las Vegas, NV USA at an elevation of 970 m. The site lies within the Nevada Test Site, administered by the US Department of Energy and has been protected from recreation and grazing disturbances for approximately 50 years (Jordan et al. 1999). Mean annual rainfall is 140 mm and precipitation occurs primarily as winter storms and as short, localized summer events. Temperatures range from winter minima of -10°C to summer temperatures > 47°C. The site is a *Larrea tridentata – Ambrosia dumosa* plant community and has intact biological soil crusts covering ~20% of the soil surface (Titus et al. 2002). Soils are Aridisols derived from calcareous alluvium with a loamy sand texture (89% sand, 6% silt and 5% clay). Subsoils lack a caliche layer, resulting in well-drained soils. Soil pH, measured in water, at the site ranges from 9-11 and soils are spatially heterogeneous in nutrients, texture and infiltration (Romney et al. 1980).

The site was established in April 1997 and consists of nine 23m plots, three control plots that are fumigated with ambient $CO_2$ concentrations (~380 ppm) and three elevated $CO_2$ plots fumigated with approximately 1.5 x ambient $CO_2$ concentrations (~550 ppm) and three plots that receive no fumigation. Few differences have been detected between the fumigated and non-fumigated controls therefore

measurements in this study only include the fumigated control and elevated $CO_2$ plots. Fumigations are delivered using the FACE technology developed by Brookhaven National Laboratory (Hendrey and Kimball 1994, Jordan et al. 1999). Plots are designed with an elevated platform system that allows researchers access without touching the soil surface, thus limiting disturbance of biological soil crusts (Jordan et al. 1999). The elevated $CO_2$ treatment ended in June 2007 and 2/3 of each plot was harvested between August and November 2007.

*Sampling and Experimental Design*

Soil fluxes were measured using collars, 25.5 cm diameter and 15 cm tall that had been installed approximately 7.5 cm into the soil in February 1999 (Billings et al. 2002a). Collars were perforated belowground to allow for penetration by roots and lateral movement of water. There were a total of eight collars located in each plot, two in each of the following cover types: under the evergreen shrub *L. tridentata* (creosote bush), under the drought deciduous shrub *Lycium* spp., under the $C_4$ bunchgrass *Pleuraphis rigida* (big gaelleta), and in plant interspaces. Following the end of $CO_2$ fumigation in June 2007, collars within each plot were relocated into the unharvested portion of the plot, four each under *L. tridentata* and in plant interspaces. Reactive N gas flux measurements (NO, $NO_y$, and $NH_3$) were made as part of 6 sampling trips during the $CO_2$ fumigation period (April 2005, July 2005, July 2006, January 2007, and March 2007) and 5 sampling trips after the end of the $CO_2$ fumigation (July 2007, October 2007, January 2008, and April 2008). Nitrous oxide measurements were made starting in July 2006. An 8.7 mm rain event interrupted sampling during July 2005, resulting in pre and post rain measurements for the elevated $CO_2$ treatment, but only post-rain measurements for the control treatment. In March 2007, sampling was conducted before and approximately 36 hours after a 30 mm artificial rain event was

applied to the plots. All nitrogen was removed from the water used for the irrigation and total dissolved inorganic nitrogen content of precipitation is typically <0.3 mg/L. Soil moisture was monitored from October 2006 through January 2008 using time domain reflectrometry probes (Dynamax, Inc, Houston, TX, USA) installed at 30cm.

*Reactive N Gas Flux Measurements*

Nitrogen gas fluxes (NO, $NO_y$, and $NH_3$) were measured using selective thermal and chemical decomposition converters to reduce or oxidize all reactive nitrogen trace gases (e.g., oxidized forms and ammonia) to NO. During measurement, a sealed opaque top with two ports was placed over the soil collar. One port remained open to the atmosphere, which minimizes induced pressure differences associated with closed chamber based measurement techniques. To make a measurement, outside air was passed, at 1 L $min^{-1}$, either directly to the measurement system to quantify background air concentrations, or through the soil collar and then to the measurement system to quantify soil emissions. The measurement system consisted of two conversion cells that coverts $NO_y$ (total oxidized N) and total reactive N ($NO_y$ + $NH_3$) to NO, respectively, and a chemiluminescence NO detector (Thermal Electron Corporation 42*i*-TL). Each converter can be isolated by Teflon valves and independent measurements made for NO (no conversion), $NO_y$ ($NO_y$ converter only), and total reactive N ($NH_3$ + $NO_y$ conversion). Fluxes were calculated based on steady-state concentrations using the equation C * q/A where C is concentration (nmol $L^{-1}$), q is the flow rate (L $s^{-1}$) and A is area ($m^2$) of the soil surface. Concentrations used for calculation were soil chamber minus air concentrations for any particular measurement. Ammonia fluxes were calculated by subtracting the total $NO_y$ value from the total reactive N value. Measurements of NO, $NO_y$ and $NH_3$ were made sequentially and total measurement time averaged 20-30 min.

The $NH_3$ conversion cell consists of a 30 cm length of nickel-chromium alloy tubing (INCONEL 600) passed through a mini tube furnace (Lindburg/Blue Mini-Mite Tube Furnace) heated to 825 ˚C. Laboratory calibrations of the converter have shown an 86% conversion efficiency for $NH_3$ with no influence on NO concentration. The $NO_y$ converter is a heated glass catalytic converter that contains a 60-cm piece of ¼" gold tube heated to 300°C. A small flow of $H_2$ (30 mL $min^{-1}$) is introduced just prior to the heated region to facilitate the reduction of oxidized N to NO. Laboratory calibration tests have shown a 100% conversion of $NO_2$ and HONO and conversion efficiencies between 78 – 99% for other components of $NO_y$ (i.e., peroxyacetyl nitrate, alkyl nitrate, $HNO_3$ and other forms of $NO_y$).

After conversion (or directly in the case of the NO only measurement), air is passed through an NO analyzer (Thermo Electron Corporation, Model 42*i* TL). This instrument detects light from the chemiluminescence reaction between NO and $O_3$:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\upsilon$$

The analyzer avoids interferences (a common problem with many NO analyzers) using a pre-reaction chamber where $O_3$ is used to consume NO before entering the reaction chamber. Because the rate of reaction with NO is very fast and the reaction with most interference compounds is relatively slower, two sequential runs (the first utilizing the pre-reaction cell and second going directly to the sample cell without pre-reaction) allows for the quantification of NO independent of all interferences and gives the instrument a detection limit of 50 pptv. The instrument was calibrated by sequential dilution of an NO standard (Scott Specialty Gases, Irvine, CA) daily.

*$N_2O$ Flux Measurements*

Fluxes of $N_2O$ were measured using a closed chamber method in which collars were sealed with a transparent, gas tight lid fitted with a septum. Three gas samples

were collected over a 2-hour period in pre-evacuated 22 mL vials and analyzed at Cornell University using a gas chromatograph fitted with an electron capture detector (Shimadzu GC-2014). Volume measurements for each chamber were made in the field. Fluxes were calculated based on the rate of increase in concentration over time, in cases where concentrations plateaued, fluxes were calculated using the slope of the initial linear period.

*Statistical Analysis*

We used analysis of variance (PROC MIXED, SAS 9.1) with a Tukey post hoc test to for a significant effect of elevated $CO_2$ on N gas emissions as well as the significance of season and cover type. All analyses were performed using SAS statistical software (Cary, NC). Statistical significance was determined at $\alpha = 0.05$. Errors are presented as ±1 SE.

**Results**

Across $CO_2$ treatments there were strong seasonal patterns in reactive N gas loss ($p < 0.05$) (Figure 3.2). High N gas loss rates were also observed periodically in the spring and fall when temperatures were moderate (average daily temperatures of 15-19 °C) and recent precipitation, either natural or artificial, resulted in high soil moisture (~11-13 % volumetric water content). High soil moisture alone was not enough to yield large losses of reactive N, winter fluxes were consistently low (<0.01-1 ng N $m^{-2}$ $s^{-1}$) and the magnitude of emissions was insensitive to extreme differences in soil moisture between 2007 and 2008 sampling dates. During periods where N gas emissions were large there were significant spatial patterns in N gas loss with the highest fluxes occurring under the dominant shrub *L. tridentata* ($p < 0.05$). Soil microsites associated with other cover types were not significantly different from each other and were combined for clarity.

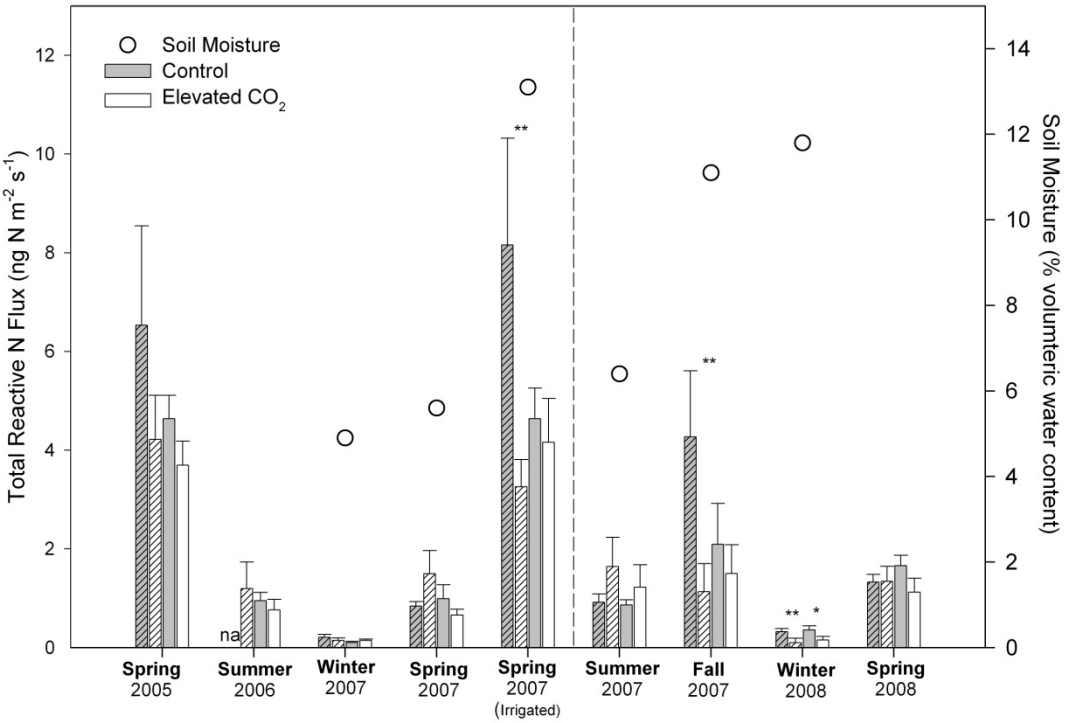


**Figure 3.2** Total reactive N gas fluxes from soils exposed to ambient and elevated $CO_2$ treatments. Hatching indicates measurements made under the dominant shrub *L. tridentata*, plain bars indicate measurements made in non-shrub influenced soils. The dashed line indicates the end of the $CO_2$ fumigation period. Differences between control and elevated $CO_2$ within a sampling period are indicated (** indicates $p < 0.05$, * indicates $p < 0.1$).

Responses to elevated $CO_2$ exposure were closely linked to seasonal and spatial patterns in reactive N gas loss, with significant reductions in N gas loss under elevated $CO_2$ occurring under shrubs during periods of high soil moisture and low to moderate soil temperature (Figure 3.2). Significant reductions in total reactive N loss were observed under *L. tridentata* under ambient soil conditions in fall 2007 and winter 2008 as well as following irrigation in spring 2007, all periods when soil moisture content was at peak values ($p < 0.05$). Reactive N losses were also lower in non-*Larrea* soils during winter 2008 ($p = 0.07$), however, at all other times N gas fluxes were insensitive to elevated $CO_2$ in non-*Larrea* soils. Changes in N gas loss were highest when temperatures were moderate, with reductions of 3-5 ng N $m^{-2}$ $s^{-1}$ during the spring and fall, compared to ~ 0.2 ng N $m^{-2}$ $s^{-1}$ in winter. Reactive N gases

were insensitive to elevated $CO_2$ exposure when soil moisture was low and during the extremely high temperatures occurring in the summer months. Reactive N gas losses were also unaffected by elevated $CO_2$ following a summer precipitation event that yielded a large pulse of reactive N gases, with maximal losses of 40.1±7.6 ng N $m^{-2}$ $s^{-1}$ (under *Larrea*) and 16.1±1.7 ng N $m^{-2}$ $s^{-1}$ (other cover types) (Figure 3.3). The observed responses to elevated $CO_2$ spanned a time period before and after the end of the $CO_2$ fumigation, indicating that changes in N gas loss were indirect responses to long-term elevated $CO_2$ exposure; however, from this experiment it is not clear how long the legacy of elevated $CO_2$ will impact losses of reactive N gases.

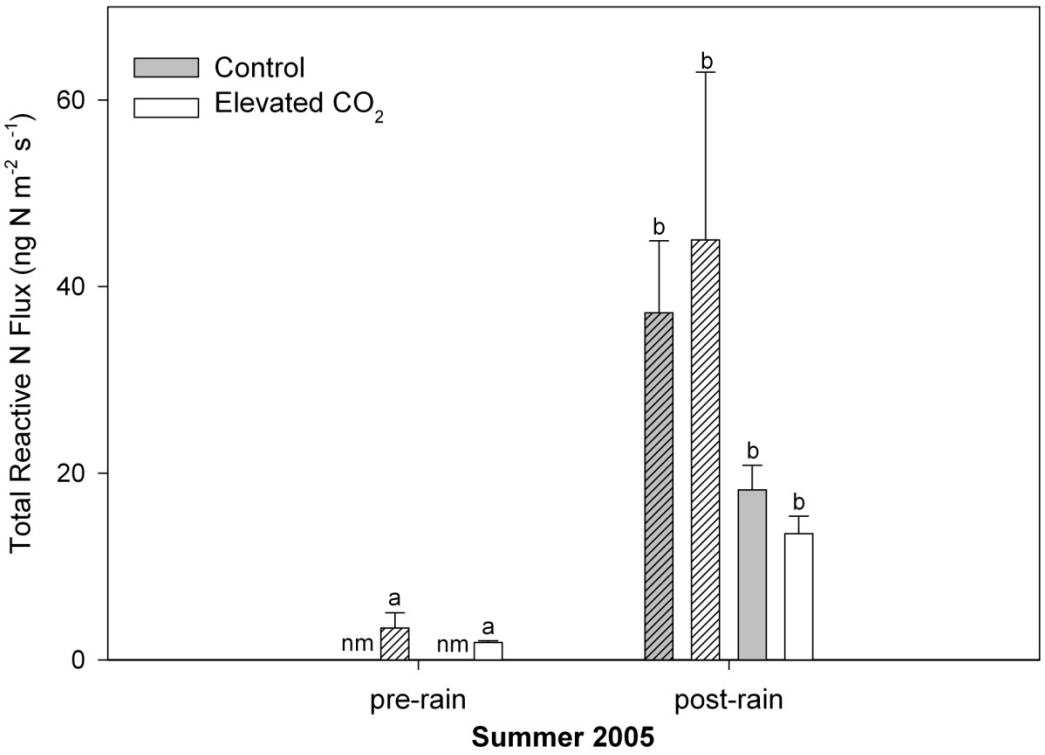


**Figure 3.3** Total reactive N gas fluxes from ambient and elevated $CO_2$ soils before and after a natural summer rain event (8.7 mm). Hatch marks indicate measurements made under the dominant shrub *L. tridentata*, plain bars indicate measurements made in non-shrub influenced soils. Precipitation occurred during the sampling period, limiting replication and treatment representation of pre-rain fluxes. Letters indicate significant differences in reactive N gas efflux ($p < 0.05$).

Reductions in reactive N gas loss under elevated $CO_2$ were observed in NO, $NO_y$ and $NH_3$ efflux (Figure 3.4). Changes in total reactive N gas loss under elevated

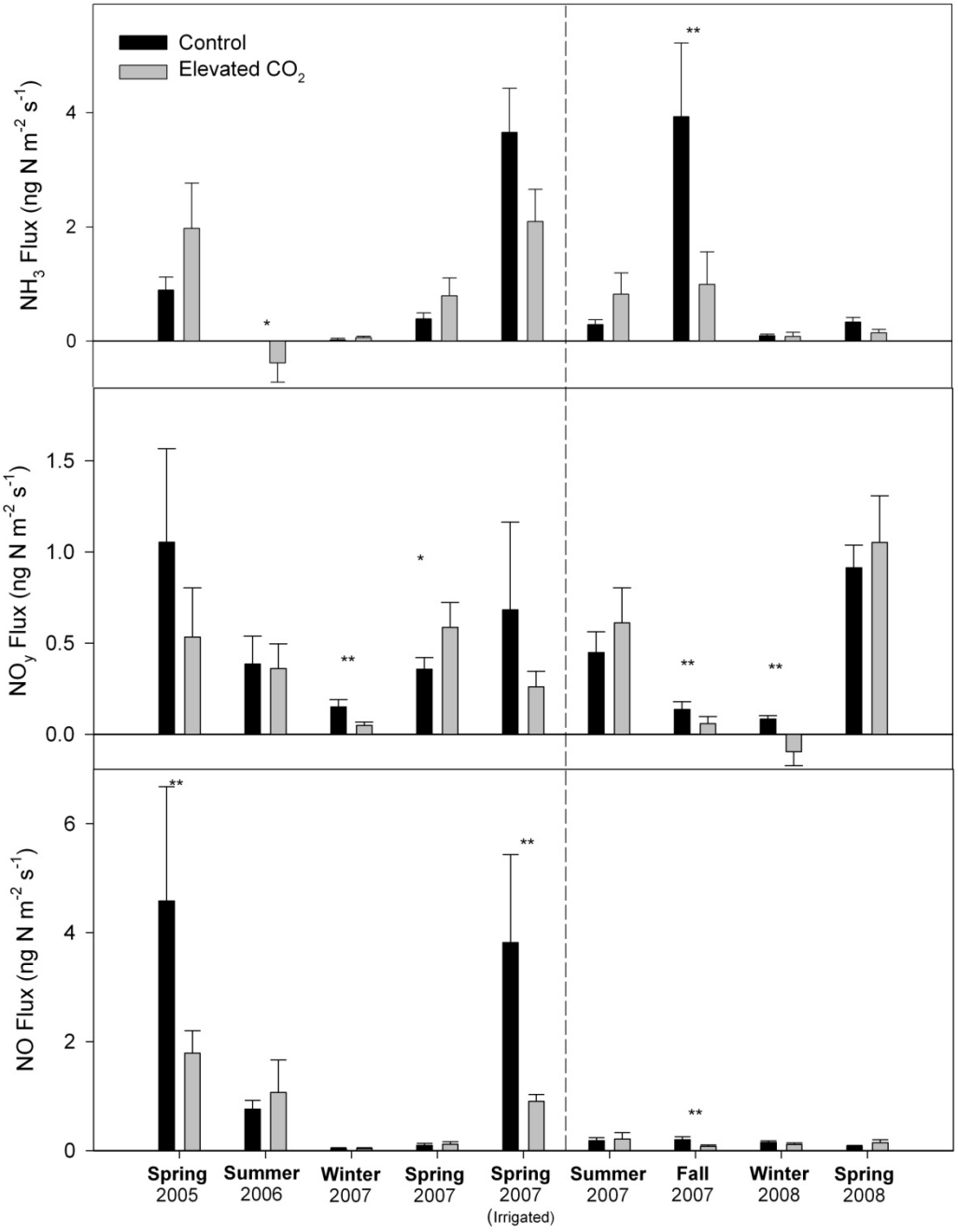


**Figure 3.4** NO, $NO_y$, and $NH_3$ emissions from *L. tridentata* soils exposed to ambient and elevated $CO_2$ treatments. The dashed line indicates the end of the $CO_2$ fumigation period. Differences between control and elevated $CO_2$ within a sampling period are indicated (** indicates $p < 0.05$, * indicates $p < 0.1$).

$CO_2$ following an artificial rain event in spring 2007 were driven by reductions in NO emissions ($p < 0.01$). Additionally, during an El Nino year (2005), significant reductions in NO gas production were also observed in the spring ($p = 0.01$). While significant reductions in NO efflux also occurred in fall 2007 ($p = 0.01$), changes in total reactive N gas loss were primarily driven by a large decrease in $NH_3$ emissions under elevated $CO_2$ ($p = 0.02$). In the winter months, changes in reactive N gas loss under elevated $CO_2$ were the result of small, but significant reductions in $NO_y$ losses. Reductions in $NO_y$ efflux occurred under *L. tridentata* during both the winter of 2007 and 2008 ($p < 0.05$); however, the responses were only large enough in 2008 to significantly impact total reactive N loss.

Emissions of $N_2O$ were a very small component of gaseous N loss and fluxes were largely insensitive to elevated $CO_2$ (Table 3.1). Across all seasons and treatments, $N_2O$ fluxes averaged 2.6±0.3 ng N $m^{-2}$ $h^{-1}$ or approximately 0.0007 ng N $m^{-2}$ $s^{-1}$ with the largest measured fluxes of $N_2O$ being 2 orders of magnitude lower than the smallest fluxes of other gaseous N species. Under most measurement conditions, $N_2O$ emissions were undetectable, with fluxes being below the detection limit of our system for 211 of 365 measurements. Maximal $N_2O$ losses occurred in the winter of 2007 and these relatively high losses (~ 0.1 ng N $m^{-2}$ $s^{-1}$) were not isolated to a single cover type or $CO_2$ treatment. Across all seasons and cover types, the only response of $N_2O$ emissions to elevated $CO_2$ was a flux increase under *L. tridentata* in the winter of 2008 ($p = 0.03$).

**Table 3.1** Mean rates of $N_2O$ fluxes from soils exposed to ambient and elevated $CO_2$ treatments. Errors are one standard error of the mean, significance differences between control and elevated $CO_2$ within a sampling period are indicated ($p < 0.05$).

| | $N_2O$ flux (ng N $m^{-2}$ $h^{-1}$) | | | |
|---|---|---|---|---|
| | *Larrea tridentata* | | *Non-Larrea* | |
| | Ambient | Elevated $CO_2$ | Ambient | Elevated $CO_2$ |
| Summer 2006 | 0.62 ± 0.28 | 0.00 ± 0.00 | 2.93 ± 1.17 | 2.63 ± 1.52 |
| Winter 2007 | 5.79 ± 4.18 | 7.52 ± 7.52 | 6.82 ± 3.48 | 8.88 ± 3.32 |
| Spring 2007 | 1.41 ± 1.07 | 2.80 ± 1.40 | 2.13 ± 0.74 | 1.83 ± 0.69 |
| Spring 2007 (irrigated) | 4.34 ± 2.48 | 2.07 ± 1.34 | 3.38 ± 0.84 | 2.77 ± 0.87 |
| Summer 2007 | 1.39 ± 0.53 | 0.91 ± 0.49 | 1.18 ± 0.57 | 1.66 ± 1.29 |
| Fall 2007 | 4.69 ± 1.05 | 4.31 ± 1.11 | 4.51 ± 1.38 | 2.77 ± 1.02 |
| Winter 2008 | 0.17 ± 0.12 | 2.66 ± 1.35* | 0.23 ± 0.18 | 1.29 ± 0.74 |
| Spring 2008 | 0.71 ± 0.52 | 0.00 ± 0.00 | 0.71 ± 0.52 | 0.89 ± 0.65 |

**Discussion**

Long-term exposure to elevated $CO_2$ altered reactive N gas emissions from Mojave Desert soils, indicating changes in the cycling and availability of N. Under soil conditions that are optimal for biological activity, moderate temperature and high moisture, long-term fumigation with elevated $CO_2$ yielded reductions in reactive N gas loss in the islands of fertility created by the dominant shrub *L. tridentata*. Decreased N gas loss under elevated $CO_2$ was characterized by large reductions in NO and $NH_3$, which suggests a change in $NH_4^+$ availability for nitrification and volatilization. We propose that these shifts in N dynamics could be driven either by reductions in availability or increases in consumption of N substrate during periods of high biological activity. Such responses could arise from decreased organic N supply from

litter, roots or N fixation, decreased N mineralization and nitrification, and/or increased N uptake (Fig. 1).

One potential mechanism for the observed reductions in gaseous N loss under elevated $CO_2$ is decreased N supply limiting substrate for $NH_3$ volatilization and NO production during nitrification (Fig. 1). However, studies on the dominant sources of N into these soils: litter, fine root turnover and N fixation in biological soil crusts all show that elevated $CO_2$ has little to no effect on these processes in the Mojave Desert. Measurements of leaf litter chemistry at the Desert FACE site show no changes in response to elevated $CO_2$ (Billings et al. 2003b) or a small increase in C:N (Weatherly et al. 2003). Additionally there is no evidence of changes in litter inputs or decomposition rates in this desert ecosystem following long-term exposure to elevated $CO_2$ (Weatherly et al. 2003). It has been proposed that changes in fine root dynamics can provide important explanatory power in understanding responses of below-ground N cycling to elevated $CO_2$ (Zak et al. 2000). In the Mojave Desert, exposure to elevated $CO_2$ did not alter fine root standing stock, production or mortality beneath shrubs (Phillips et al. 2006); however, we have no information about the response of other root derived inputs of nutrients such as rhizodeposition of labile substrates. Additionally, changes in new N inputs from N fixation under elevated $CO_2$ could also directly impact the processes that drive N gas production; however, multiple measurements of N fixation rates in this system show no changes in response to elevated $CO_2$ (Billings et al. 2003a, Schaeffer et al. 2007).

The lack of a response to elevated $CO_2$ of multiple factors influencing N availability in desert soils suggests that change in internal N cycling are responsible for growing season reduction in N gas loss from Mojave soils. Mineralization of organic N to $NH_4^+$ provides the substrate for $NH_3$ volatilization as well as NO production through nitrification (Fig. 1). Changes in mineralization rates could

therefore drive shifts in reactive N gas loss under elevated $CO_2$. Consistent with this hypothesis, Jin and Evans (2007) found decreased gross mineralization rates during the late spring under elevated $CO_2$ in the Mojave Desert. These gross mineralization rates provide an overall metric for the movement of $NH_4^+$ through the soil N pool and therefore the total potential for NO and $NH_3$ loss. We would predict that reductions NO and $NH_3$ emissions would also correspond to reductions in net mineralization rates, which represent the balance between microbial mineralization and consumption of $NH_4^+$, however, either no change in net mineralization (Billings et al. 2002a) or an increase in potential net mineralization under elevated $CO_2$ (Schaeffer et al. 2007) have been reported for this system. Additionally, biological NO production is likely to be the result of nitrification in deserts (Hartley and Schlesinger 2000, Parton et al. 2001, McCalley and Sparks 2008) and should reflect nitrification responses to elevated $CO_2$ (Fig 1). Laboratory measurements of potential net nitrification in desert FACE soils yield results consistent with reductions in nitrification rates lowering NO emissions during periods of microbial activity (Schaeffer et al. 2007). Gross rats of nitrification, which quantify the total amount of nitrification and therefore potential for NO production, show a somewhat conflicting pattern, with some evidence for increased rates under elevated $CO_2$ in interspace, but not shrub soils (Jin and Evans 2007). Given the high spatial and temporal variability in nutrient dynamics in desert ecosystems (Titus et al. 2002, Jin and Evans 2007) it is not surprising that there are some inconsistencies in N cycling responses to elevated $CO_2$, however, overall responses at the Desert FACE site support the hypothesis that reductions in reactive N gas emissions under elevated $CO_2$ reflect decreased mineralization as well as the subsequent nitrification of $NH_4^+$.

The observed reductions in N gas loss due to changes in mineralization and nitrification under elevated $CO_2$ should be related to alterations in plant and microbial

demand for and uptake of N. This is because in the absence of changes in N supply to the soil, reduced availability of $NH_4^+$ for nitrification and volatilization indicates increased retention of N in microbial or plant biomass (Fig. 1). At the Desert FACE site, increases in shrub productivity and annual biomass under elevated $CO_2$ have been observed during periods of high water availability (Smith et al. 2000, Housman et al. 2006), potentially increasing plant N demand during periods of peak biological activity. In the microbial community, meta-analysis of the effects of elevated $CO_2$ on soil nutrient dynamics shows that increases in immobilization of N linked to increased microbial N demand is a common response to elevated $CO_2$ across a wide range of ecosystems (de Graaff et al. 2006). In the Mojave Desert, $^{15}N$ enrichment of *L .tridentata* leaves growing under elevated $CO_2$ indicates increased microbial activity and N immobilization consistent with increased retention of N by the microbial community. Direct measurements of microbial biomass N in these soils, however, have provided inconsistent results, showing increases (Schaeffer et al. 2007) and decreases (Jin and Evans 2007). We know that the availability of carbon substrate can limit microbial activity in the Mojave Desert (Schaeffer et al. 2003) and that additions of labile C sources cause increased N immobilization (Schaeffer et al. 2003) and decreased NO and $NH_3$ efflux (McCalley and Sparks 2008) similar to what we see under elevated $CO_2$. Therefore observations of increased availability of labile C in soils exposed to elevated $CO_2$ (Schaeffer et al. 2007) potentially due to increased rhizodeposition by shrubs (Nguyen 2003) provides a mechanism by which elevated $CO_2$ changes resources for microbial metabolism under shrubs, increasing demand for and immobilization of N, ultimately lowering gaseous N losses.

The Mojave Desert is not unique in that long-term exposure to elevated $CO_2$ can cause reductions in gaseous N loss due to alterations in microbial utilization of N. Measurements of reactive N gas emissions under elevated $CO_2$ are limited; however,

patterns similar to what we see in the Mojave Desert have been documented in other systems. When exposed to elevated $CO_2$ and given nutrient subsidies, grassland ecosystems in both California and Colorado exhibited increases in N immobilization coupled with substantial decreases in nitrification and NO efflux (Hungate et al. 1997, Mosier et al. 2003). There is a lack of data on responses of reactive N gas loss to elevated $CO_2$ across a wide range of ecosystems, however, the variability in responses of N cycling to elevated $CO_2$ suggests that changes in reactive N efflux will be equally variable (Zak et al. 2000, de Graaff et al. 2006). Generalized responses of increased N immobilization (de Graaff et al. 2006) and soil respiration (Zak et al. 2000) could indicate widespread reduction in substrate availability for processes that yield reactive N, however, documentation of both increases and decreases in mineralization and nitrification rates under elevated $CO_2$ indicate that processes underlying reactive N gas loss have the potential to positively or negatively change gas fluxes under elevated $CO_2$ (Hungate et al. 1999, Carnol et al. 2002, Barnard et al. 2004, Barnard et al. 2005, Langley et al. 2009, Muller et al. 2009).

Alterations in N gas loss under elevated $CO_2$ are associated with changes in biological cycling of N, however, when studying reactive N loss in arid ecosystems it is important to acknowledge that in these environments the majority of N loss can occur through abiotic processes associated with extreme summertime surface temperatures (McCalley and Sparks 2009), which did not respond to elevated $CO_2$ in our study. This suggests that the largest perturbation to gaseous N losses in arid systems would result from changes in summer N loss dynamics, particularly the frequency of summer rain events that yield large pulses of N loss. Our data indicates that while growing season emissions of NO and $NH_3$ can be substantially altered by rising atmospheric $CO_2$ concentrations, these larger summertime losses, including the large pulses of N gas emissions following monsoonal rain events are not affected by

elevated $CO_2$. Summer fluxes result from chemical formation of reactive N, which utilize soil stocks of inorganic and/or organic N and are maximized under high soil moisture and temperature conditions (McCalley and Sparks 2009). Insensitivity of this loss mechanism is likely due to chemical losses not being substrate limited and instead largely being determined by physical conditions, with temperature and precipitation being the primary determinant of flux rates. Although we expect that this loss mechanism is highly sensitive to changes in summer temperature and precipitation predicted to occur along with rising atmospheric $CO_2$ concentrations (Solomon et al. 2007), changes in soil N pools during 10 years of exposure to elevated $CO_2$ are not enough to alter the rate of these reactions.

Combining seasonal measurements of reactive N gas emissions and our understanding of the response of other ecosystem parameters to elevated $CO_2$ provides important insights into the nature of desert responses to global change. Our results provide supporting evidence that elevated $CO_2$ alters soil N dynamics in arid ecosystems. Reductions in NO and $NH_3$ efflux during periods of peak biological activity point towards increased N uptake and decreased N mineralization and nitrification as dominant changes to soil nutrient cycling under elevated $CO_2$. Ultimately these alterations in reactive N gas efflux have important implications for nutrient availability and biosphere-atmosphere interactions in arid regions. Specifically, changes in plant and microbial demand for N under elevated $CO_2$ reduces reactive N gas fluxes during periods of peak N demand, increasing the retention of biologically available N during critical growth periods. Given that annual emissions of reactive N gases are approximately 1 kg N $ha^{-1}$ in the Mojave Desert (McCalley and Sparks 2008) a magnitude that is roughly equivalent to 20-25% of the total N taken up by plants annually (Rundel and Gibson 1996), changes in this flux represents a small, but biologically relevant alteration in N losses from a resource poor desert ecosystem.

Conversely these responses alter the flux of new reactive gases into the atmosphere, reducing NO and/or $NH_3$ efflux and potentially impacting local atmospheric processes in otherwise pristine and remote desert regions.

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# CHAPTER 4

# DAILY, SEASONAL, AND ANNUAL PATTERNS OF REACTIVE NITROGEN GAS EMISSIONS FROM MOJAVE DESERT SOILS


## Abstract

Soil emissions of N gases are an important component of desert N dynamics, often representing the primary N loss mechanism in many water-limited ecosystems. In arid and semi-arid regions, fluxes of reactive N gases are sensitive to environmental conditions including temperature and moisture, which exhibit substantial temporal variability. In the work presented here, we characterize daily, seasonal and annual patterns in N gas emissions from Mojave Desert soils and then use that information to estimate the annual losses for this ecosystem. We estimated total reactive N gas efflux by quantifying nitric oxide (NO), other nitrogen oxides ($NO_y$) and ammonia ($NH_3$). Across all measurements, NO was <50% of the total flux and both $NO_y$ and $NH_3$ were important components of gaseous N emissions. We found a clear diurnal pattern in soil emissions with fluxes peaking at midday. This pattern was evident during all seasons, however, it was most pronounced in the summer where fluxes ranged from <0.1-7.6 ng N $m^{-2}$ $s^{-1}$ across a single day. Seasonal measurements showed minimal losses during the winter and larger, highly variable losses during warmer parts of the year. During times of high biological activity in the spring and fall, daily N fluxes ranged from 0.009 mg N $m^{-2}$ $d^{-1}$ during a dry year to 0.17 mg N $m^{-2}$ $d^{-1}$ during a wet, El Ninõ year. In comparison, dry summer soils exhibited an average flux of 0.06 mg N $m^{-2}$ $d^{-1}$, suggesting the importance of abiotic processes driving N gas loss from desert soils during times of limited biological activity. Further, large pulses of reactive N gases were observed following summer precipitation events with emissions ranging from 0.21 mg N $m^{-2}$ for small events (1-2 mm) to 6 mg $m^{-2}$ for large events (>20 mm).

As opposed to a single post-rain peak in N emissions, pulses of reactive N gas following precipitation were characterized by a series of declining diurnal cycles as soils dried, with the time to return to background levels ranging from 1-5 days. Combining seasonal patterns of N gas efflux and post-rain N pulses with existing precipitation records yielded annual estimates of reactive N gas efflux that ranged between 0.1 and 0.6 kg N $ha^{-1}$ $y^{-1}$. Variation in annual emissions was primarily driven by year-to-year variation in precipitation, demonstrating the impact that alterations in precipitation patterns under future climate scenarios will have on N dynamics in water limited ecosystems.

**Introduction**

The long-term balance between N inputs and losses is an important constraint to biological activity in arid regions because, after access to water, nitrogen availability often most limits productivity (Whitford 2002). Gaseous emissions from soil are thought to be the primary form of N export in arid lands and loss estimates range from <1-3 kg N $ha^{-1}$ $y^{-1}$ in arid regions of North America and Africa (Peterjohn and Schlesinger 1990, Davidson and Kingerlee 1997, Feig et al. 2008). However, these loss estimates are most often generated as the residual of a mass balance rather than direct measurements. Soil emissions of N are closely linked to moisture and temperature (Ludwig et al. 2001, Galbally et al. 2008) and, hence, there is a strong potential for N loss dynamics to be highly sensitive to climate conditions. Therefore, alterations in precipitation patterns as a result of climate change could have pronounced impacts on gaseous N losses from desert ecosystems. However, while climate models predict future shifts in the timing and/or amount of precipitation, there is little consensus on the nature of this change (Solomon et al. 2007).

Gaseous N species emitted from soil also directly impact key atmospheric processes associated with climate and air quality. The dominant nitrogen gases produced in desert soils include nitric oxide (NO), a group of other reactive nitrogen oxides including HONO, $HNO_3$, $NO_2$ and organic oxides, which are categorized as $NO_y$, and ammonia ($NH_3$). Nitrous oxide ($N_2O$) can also be produced in soils, however, in the Mojave Desert $N_2O$ fluxes are several orders of magnitude lower that other N gas species and have a minimal impact on terrestrial or atmospheric processes (McCalley and Sparks in prep, Billings et al 2002). Nitrogen oxides (NO and $NO_y$) are a necessary precursor to ozone formation in the troposphere, a potent greenhouse gas as well as a detrimental pollutant (Crutzen 1979, Solomon et al. 2007). Ammonia also participates in chemical processes in the atmosphere including aerosol and cloud formation, which in turn impact the attenuation of radiation and the cooling of the Earth's surface (Solomon et al. 2007). The magnitude and composition of soil fluxes therefore have the potential to influence important atmospheric processes, especially in regions distant from anthropogenic sources. Although fluxes from desert environments are often small relative to other, more production ecosystems (Davidson and Kingerlee 1997), the reactivity of nitrogen oxides and ammonia in the atmosphere means that these natural sources can have important impacts on regional atmospheric processes (Honrath et al. 2000).

Production of nitrogen gases in soils occurs through several different pathways all of which are sensitive to daily, seasonal and annual variation in environmental conditions including temperature and precipitation. Nitric oxide is the product of the microbe-mediated processes of nitrification and denitrification (Firestone and Davidson 1989) and $NH_3$ efflux is the result of the chemical transformation of mineralized $NH_4^+$ under the basic soil conditions prevalent in arid regions (Schlesinger and Peterjohn 1991). In desert soils, nitrogen oxides and $NH_3$ are also produced via

abiotic processes associated with high surface soil temperatures and this mechanism can yield substantial summertime losses, especially following precipitation (McCalley and Sparks 2009). Gaseous N losses associated with nitrification and denitrification rates are controlled by factors that include the concentration of inorganic N ($NO_3^-$ and $NH_4^+$), soil moisture, temperature, accessibility of labile C, and physical soil properties (Robertson and Tiedje 1987, Parton et al. 2001). As with nitrification, $NH_3$ volatilization is dependent on $NH_4^+$ concentrations, with the mineralization of $NH_4^+$ from soil organic matter being a primary control on $NH_3$ fluxes (Schlesinger and Peterjohn 1991, Austin et al. 2004, McCalley and Sparks 2008).

In the past decade, multiple estimates for reactive N gas loss have been generated for arid and semi-arid ecosystems (Galbally et al. 2008); however, these studies have been challenged by a lack of adequate information needed to generate an accurate annual estimate. Most studies quantify losses of a single gas species, mostly notably NO, however recent research has identified that NO is only one of several reactive N gas species produced in desert soils (McCalley and Sparks 2008, 2009). A broader analytical approach that simultaneously quantifies multiple gas species is necessary to fully capture N loss dynamics in these regions. Further, calculations of annual N gas efflux are most often based on measurements made within a single year or sometimes even a single or few seasons. This may be a reasonable strategy in many ecosystems, however, one that is incompatible with the highly variable precipitation regimes that characterize many arid ecosystems (Blainey et al. 2007). Annual variation in rainfall is a central parameter in determining plant productivity and ecosystem processes in desert environments (Noy-Meir 1973), yet our understanding of N gas fluxes from these regions are derived from measurements made within a single year.

The goal of this project was to generate a robust estimate of annual N losses from the Mojave Desert that both incorporated measurements of total reactive N gas

species and considered the role of natural climatic fluctuations in influencing the magnitude of N gas emissions. We addressed this goal by identifying the influence of daily, seasonal and annual variability in environmental conditions on fluxes of reactive N gases from desert soils. To fully characterize N loss patterns and develop an estimate for total reactive N loss we utilized a multi-year data set that included (1) daily flux patterns driven by diurnal variation in surface soil temperature, (2) a range of winter and 'growing season' soil moisture conditions, and (3) pulses associated with different sizes and frequencies of summer rain events. We hypothesized that the magnitude of annual N gas emissions would be driven by pulses of reactive N gas efflux following summer precipitation events and that inter-annual variation in the amount and timing in precipitation would yield a large range in annual emissions across years, suggesting that global climate change could substantially impact soil N emissions from desert ecosystems.

## Methods

### *Study Site*

Measurements were conducted at the Nevada Desert FACE Facility (NDFF) and Mojave Global Change Facility (MGCF) in Nye County, Nevada (36°49'N, 115°55'W), 90 km northwest of Las Vegas, NV USA at an elevation of 970 m. These sites lie within the Nevada Test Site, administered by the US Department of Energy and have been protected from recreation and grazing disturbances for approximately 50 years (Jordan et al. 1999). Mean annual rainfall is 140 mm and precipitation occurs primarily as winter storms and as short, localized summer events with approximately 60% of annual precipitation occurring during the winter and 40% in the summer (Blainey et al. 2007). Temperatures range from winter minima of -10°C to summer temperatures > 47°C. The site is a *Larrea tridentata – Ambrosia dumosa* plant

community and has intact biological soil crusts covering ~20% of the soil surface (Titus et al. 2002). Soils are Aridisols derived from calcareous alluvium with a loamy sand texture (89% sand, 6% silt and 5% clay). Subsoils lack a caliche layer, resulting in well-drained soils. Soil pH, measured in water, at the sites range from 9-11 and soils are spatially heterogeneous in nutrients, texture and infiltration (Romney et al. 1980).

*Sampling and Experimental Design*

Soil fluxes were measured using collars, 25.5 cm diameter and 15 cm tall that had been installed approximately 7.5 cm into the soil in February 1999 (Billings et al. 2002) at the NDFF, June 2004 at the MGCF, and in a region adjacent to the NDFF in April 2008 and 2009. In total, data for this project were collected from 84 soil collars. Collars were installed in a range of cover types representative of the spatial heterogeneity characteristic of this ecosystem, including: under the evergreen shrub *Larrea tridentata* (creosote bush), adjacent to the drought deciduous shrub *Lycium* spp., adjacent to the $C_4$ bunchgrass *Pleuraphis rigida* (big gaelleta), and in plant interspaces. Collars were considered as two cover types in the present analysis, beneath *L. tridentata* and plant interspaces, due to the lack of a significant effect of proximity to other plant species (McCalley and Sparks 2008).

Reactive N gas flux measurements (NO, $NO_y$, and $NH_3$) were made as part of 11 sampling trips between the spring of 2005 and summer of 2009 (April 2005, July 2005, July 2006, January 2007, March 2007, July 2007, October 2007, January 2008, April 2008, July 2008, June 2009). In addition to daytime measurements made between approximately 8am and 6pm, diurnal measurements starting several hours before sunrise and ending several hours after sunset were made (January 2007, March 2007, July 2007, and April 2008), as well as post-irrigation measurements (10 mm:

June 2009, 25-30 mm: January 2007, March 2007, July 2007, October 2007, January 2008, April 2008, July 2008), and measurements made following natural rain events (1.7 mm: July 2006, ~ 1-2 mm: June 2009, 8 mm: July 2005). Artificial irrigations were always applied in the evening and were either added as a localized addition to individual collars or added at the plot level using a sprinkler system.

Soil moisture measurements were made at the site through November 2007 using neutron probes (Model 503 Hydroprobe, Campbell Pacific Nuclear Corporation, Martinez, California) installed at 15-20 cm and between October 2006 and January 2008 using time domain refractrometry (TDR) probes (Dynamax, Inc, Houston, TX, USA) installed at 30 cm (Chris Holmes, personal communication). Measurements from neutron probes are reported as % soil water content and measurements from TDR probes are reported as % volumetric water content. Data from these sensors were used to provide comparative estimates for average soil moisture across sampling trips.

*Reactive N Gas Flux Measurements*

Nitrogen gas fluxes (NO, $NO_y$, and $NH_3$) were measured using selective thermal and chemical decomposition converters to reduce or oxidize all reactive nitrogen trace gases (e.g., oxidized forms and ammonia) to NO. During measurement, a sealed opaque top with two ports was placed over the soil collar. One port remained open to the atmosphere, which minimizes induced pressure differences associated with closed chamber based measurement techniques. To make a measurement, outside air was passed, at 1 L $min^{-1}$, either directly to the measurement system to quantify background air concentrations, or through the soil collar and then to the measurement system to quantify soil emissions. The measurement system consisted of two conversion cells that converts $NO_y$ (total oxidized N) and total reactive N ($NO_y$ + $NH_3$) to NO, respectively, and a chemiluminescence NO detector (Thermal Electron

Corporation 42*i*-TL). Each converter can be isolated by Teflon valves and independent measurements can be made for NO (no conversion), $NO_y$ ($NO_y$ converter only), and total reactive N ($NH_3$ + $NO_y$ conversion). Fluxes were calculated based on steady-state concentrations using the equation C * q/A where C is concentration (nmol $L^{-1}$), q is the flow rate (L $s^{-1}$) and A is area ($m^2$) of the soil surface. Concentrations used for calculation were soil chamber minus air concentrations for any particular measurement. Ammonia fluxes were calculated by subtracting the total $NO_y$ value from the total reactive N value. Measurements of NO, $NO_y$ and $NH_3$ were made sequentially and total measurement time averaged 20-30 min.

The $NH_3$ conversion cell consists of a 30 cm length of nickel-chromium alloy tubing (INCONEL 600) passed through a mini tube furnace (Lindburg/Blue Mini-Mite Tube Furnace) heated to 825 ˚C. Laboratory calibrations of the converter have shown an 86% conversion efficiency for $NH_3$ with no influence on NO concentration. The $NO_y$ converter is a heated glass catalytic converter that contains a 60-cm piece of ¼" gold tube heated to 300°C. A small flow of $H_2$ (30 mL $min^{-1}$) is introduced just prior to the heated region to facilitate the reduction of oxidized N to NO. Laboratory calibration tests have shown a 100% conversion of $NO_2$ and HONO and conversion efficiencies between 78 – 99% for other components of $NO_y$ (i.e., peroxyacetyl nitrate, alkyl nitrate, $HNO_3$ and other forms of $NO_y$).

After conversion (or directly in the case of the NO only measurement), air is passed through an NO analyzer (Thermo Electron Corporation, Model 42*i* TL). This instrument detects light from the chemiluminescence reaction between NO and $O_3$:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\upsilon$$

The analyzer avoids interferences (a common problem with many NO analyzers) using a pre-reaction chamber where $O_3$ is used to consume NO before entering the reaction chamber. Because the rate of reaction with NO is very fast and the reaction with most

interference compounds is relatively slower, two sequential runs (the first utilizing the pre-reaction cell and second going directly to the sample cell without pre-reaction) allows for the quantification of NO independent of all interferences and gives the instrument a detection limit of 50 pptv. The instrument was calibrated by sequential dilution of an NO standard (Scott Specialty Gases, Irvine, CA) daily.

*Calculations of Annual N Efflux*

Annual N efflux estimates were generated using three factors: (1) diurnal patterns of loss were quantified from dry soils during each season to provide an average daily total loss for dry soils during each season (2) based upon spot measurements taken under a range of soil moisture conditions across seasons, the dry soil estimate was adjusted for variable soil moisture conditions, and (3) post-precipitation pulses following summer rain events ranging from 1.7-30 mm were used to augment summer estimates.

(1) Curves were fit to measurements of diurnal patterns of N loss made during each season and daily N fluxes were calculated based on the area beneath these curves. Diurnal measurements included sampling of interspace and *L. tridentata* soils proportional to their relative surface coverage, accounting for spatial variability in the magnitude of N losses. Four sets of diurnal measurements were made, one winter, two spring and one summer, therefore these flux estimates did not account for the impact of inter-annual variability in moisture conditions on the magnitude of soil emissions.

(2) To account for the effect of soil moisture within a season, we compared spot measurements made across multiple years, representing a range of moisture conditions typical for the region, including low, average and high precipitation years and then used these values to proportionally adjust the total daily flux rate generated by the season-specific diurnal. For example, if spot measurements made at a higher

soil moisture content suggested a 50% greater flux at points comparable to the diurnal, then the total daily loss was increased by 50% for that soil moisture. The coverage of our dataset allowed us to make these kinds of estimates for four general soil water categories during the growing season (i.e., spring and fall): Dry (< 50% of 30 year average), Average (within ±25% of average), wet (150% of average), and very wet (> 200% of average) and two categories during the winter (Dry and Average). Only one daily flux rate was calculated for the summer due to minimal variation in summer moisture conditions except for the short period following precipitation. Pulses of N loss following summer rain events were then calculated as a separate loss term.

(3) Gaseous N losses during summer rain events were calculated from: (A) a multiple day flux pattern following a 10 mm irrigation, and (B) spot measurements made following natural and artificial rain events ranging from 1.7 to 30 mm. Diurnal curves were fit to soil flux measurements made for three days following an artificial 10 mm irrigation event. Flux measurements included sampling of interspace and *L. tridentata* soils proportional to their relative surface coverage, accounting for spatial variability in the magnitude of N losses. The total N loss associated with the post-precipitation period was calculated by integrating the area under each daily curve and extrapolating out the decline in daily N losses until emissions reached the background dry soil rates. To account for the effect of event size on post-rain N pulses, spot measurements taken following smaller and larger events were compared to the 10 mm event. These comparisons were used to modify post-rain N losses for the magnitude and duration of pulses produced by smaller and larger event sizes. For example, if the pulse within 24 hrs of a 200% larger rain event was 100% bigger, the total daily loss for each day following this larger event was increased by 100%. Larger pulses also take longer to return to background dry soil values; therefore the decline in daily pulses was extrapolated out for each event size until daily emissions reached dry soil

rates. Finally, to account for event sizes other than those we experienced in the field we assumed that intermediate event sizes would yield intermediate pulses of N gases and calculated the magnitude of post-rain N pulses for 5 event size classes (1-2 mm, 2-5 mm, 5-10 mm, 10-20 mm and >20 mm). Using the NDFF precipitation record from 1997-2007, we then calculated N losses following summer rain events across a range of naturally occurring summertime precipitation patterns.

Annual estimates were then defined as the sum of the factors described above and this summing exercise was repeated for four different soil moisture years ranging from dry (< 50% of average) to very wet (> 200% of average). For the purpose of this analysis summer was categorized as June-September, winter was November-February, and the spring/fall was March-May and October.

*Statistical Analysis*

We used analysis of variance (PROC MIXED, SAS 9.1) with Tukey post hoc tests to examine differences among season, cover type, and rain events. Curves were fit to diurnal patterns and post-rain pulses using a Marquardt-Levenberg algorithm to fit a three parameter Gaussian curve (SigmaPlot 2000). Statistical significance was determined at $\alpha = 0.05$. Errors are presented as ±1 SE.

**Results**

Diurnal measurements of total reactive N efflux in winter, spring and summer show a strong daily pattern in soil emissions, with the largest fluxes occurring at midday (Figure 4.1). Morning and evening fluxes were consistently low throughout the year; however, the magnitude of the midday peak in soil efflux varied with season. The largest peak in N gas emission occurred during the summer, with the modeled curve fit predicting a midday value of 2.67 ng N $m^{-2}$ $s^{-1}$; whereas the midday value in

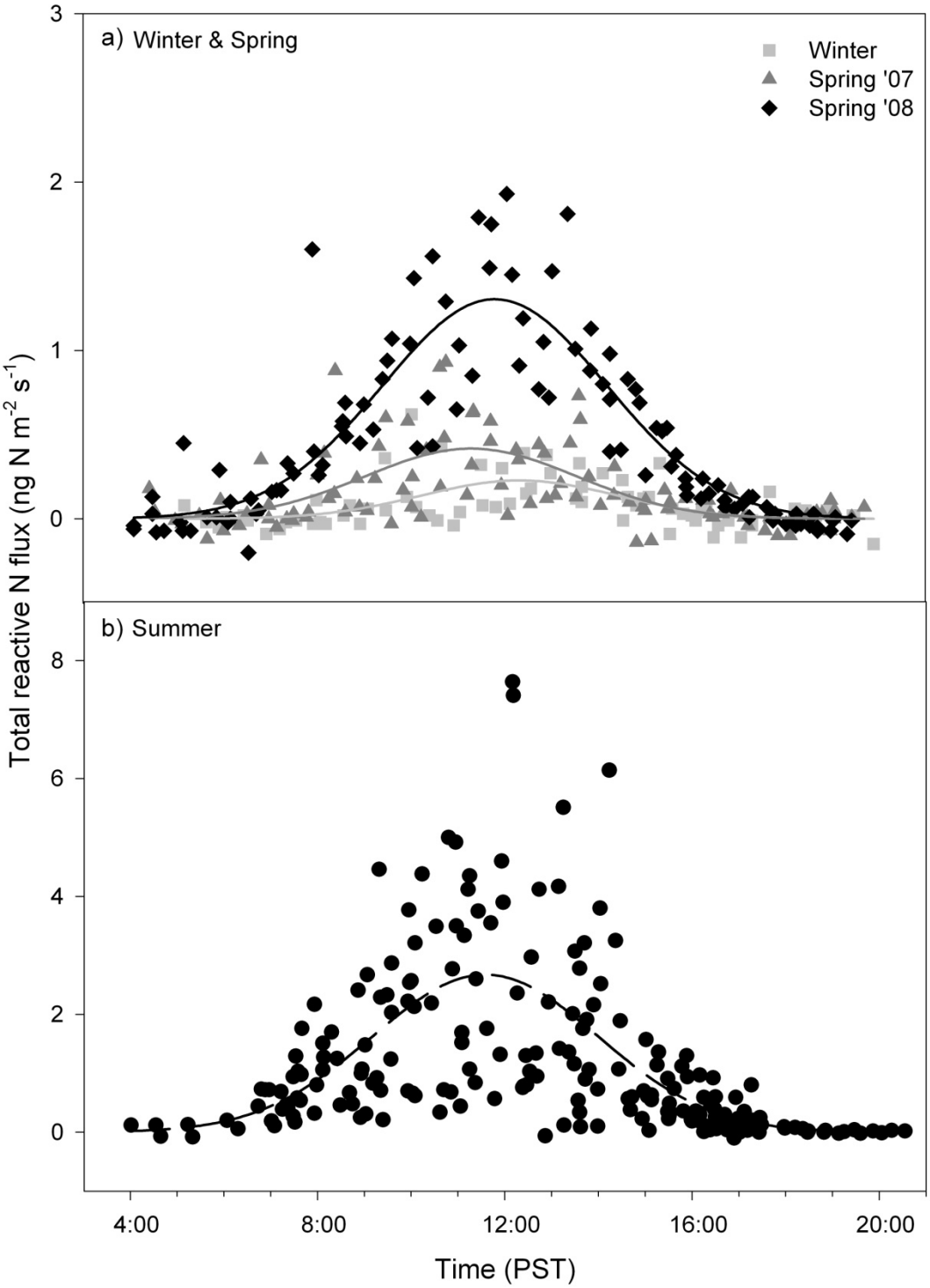


**Figure 4.1** Diurnal patterns in total reactive N gas loss during **(a)** growing season and winter months (Winter $R^2 = 0.35$, $p<0.0001$, Spring 2007 $R^2 = 0.35$, $p<0.0001$, Spring 2008 $R^2 = 0.76$, $p<0.0001$) and **(b)** Summer ($R^2 = 0.40$, $p<0.0001$).

N gas emissions during the winter was only 0.23 ng N $m^{-2}$ $s^{-1}$ and springtime midday fluxes fell between 0.42 and 1.3 ng N $m^{-2}$ $s^{-1}$. The average daily N gas emissions based on the area under the best-fit curve for each diurnal plot showed a strong seasonal pattern in soil emissions (Table 4.1). Estimated summertime N gas efflux was 0.06 mg N $m^{-2}$ $day^{-1}$, more than 10 times that for winter months and twice that of the largest loss for spring. Diurnals varied between years, for example N gas loss was more than 3 times higher in April 2008 as compared to March 2007 (Figure 4.1).

**Table 4.1** Seasonal and annual fluxes of total reactive N gases across natural climatic conditions ranging from low to high precipitation years. Winter includes November-February (120 days), growing season includes March-May and October (123 days), and summer includes June-September (122 days).

| | *Dry Year* | *Average Year* | *Wet Year* | *Very Wet Year* |
|---|---|---|---|---|
| | *Daily total reactive N flux (mg N $m^{-2}$ $d^{-1}$)*[†] | | | |
| Winter | 0.004 | --- | 0.009 | --- |
| Growing Season | 0.009 | 0.028 | 0.090 | 0.170 |
| Summer | --- | 0.058 | --- | --- |
| | *Annual total reactive N flux (kg N $ha^{-1}$ $y^{-1}$)* | | | |
| Winter | 0.005 | 0.008 | 0.010 | 0.010 |
| Growing Season | 0.023 | 0.072[‡] | 0.111 | 0.209 |
| Summer | 0.071 | 0.071 | 0.071 | 0.071 |
| Summer Precipitation[¥] | 0.006 | 0.145 | 0.233 | 0.316 |
| **Total** | **0.11** | **0.30** | **0.43** | **0.60** |

[†]Calculated based on the area under diurnal curves (dry winter, dry and average growing season, see Figure 4.1) modified by proportional differences between spot measurements made under varying moisture conditions within a season (see Figure 4. 2 and 4.3).

[‡] Average year growing season flux is calculated based on 63 days at 0.028 mg N $m^{-2}$ $d^{-1}$ and 60 wet days at 0.090 mg N $m^{-2}$ $d^{-1}$.

[¥] Calculated based on the range of N losses predicted from the precipitation record for the NDFF (see Table 4.2 for details).

There was significant variability in winter measurements of total reactive N made over two years and a range of soil water availability (Figure 4.2). Higher soil moisture conditions in 2008 resulted in significantly higher soil fluxes in interspace soils compared to 2007; however irrigation in 2008 caused a decline in fluxes, resulting in fluxes similar to those measured from dry soils in 2007. In *L. tridentata* soils, there was a trend towards increasing fluxes with increasing soil moisture.

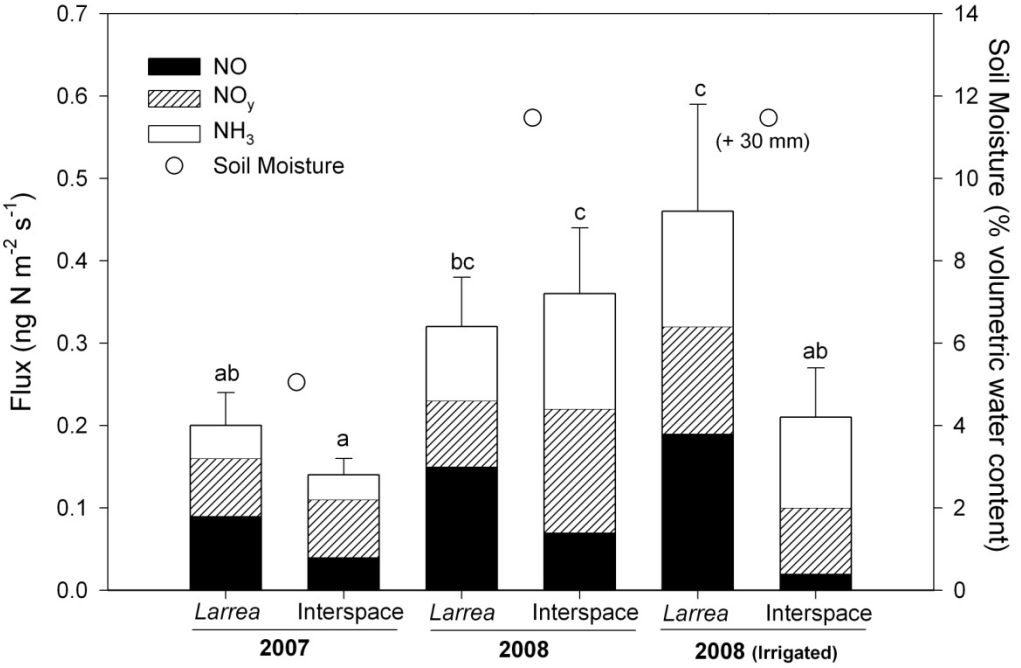


**Figure 4.2** Average daytime reactive N gas fluxes and soil moisture conditions during winter sampling periods (2007: n = 13 for *L. tridentata* and n = 46 for interspace, 2008: n = 12 for all measurements). Soil moisture content is based on TDR data from NDFF during the sampling periods; additional moisture from a localized irrigation is indicated above the background soil moisture content (eg. +30 mm indicates application of an additional 30 mm of water). Letters indicate significant differences in total reactive N gas efflux ($p < 0.05$).

Following irrigation, soil fluxes were significantly higher under *L. tridentata* compared to plant interspaces; however, there was no effect of cover type for winter measurements made under ambient moisture conditions. Nitric oxide was less than half of the total reactive N flux during the winter and overall the three gas species, NO, $NO_y$ and $NH_3$, were relatively equal components of the total flux. Across cover

types, total reactive N fluxes in 2008 were double those in 2007, yielding a daily N loss estimate of 0.009 mg N $m^{-2}$ $day^{-1}$ for winter conditions during the wetter year and a loss of 0.004 mg N $m^{-2}$ $s^{-1}$ estimated from the diurnal measurements made in the drier year of 2007 (Table 4.1).

Measurements made in the spring and fall show that soil moisture and cover type influence soil emissions across years (Figure 4.3). Measurements range from the

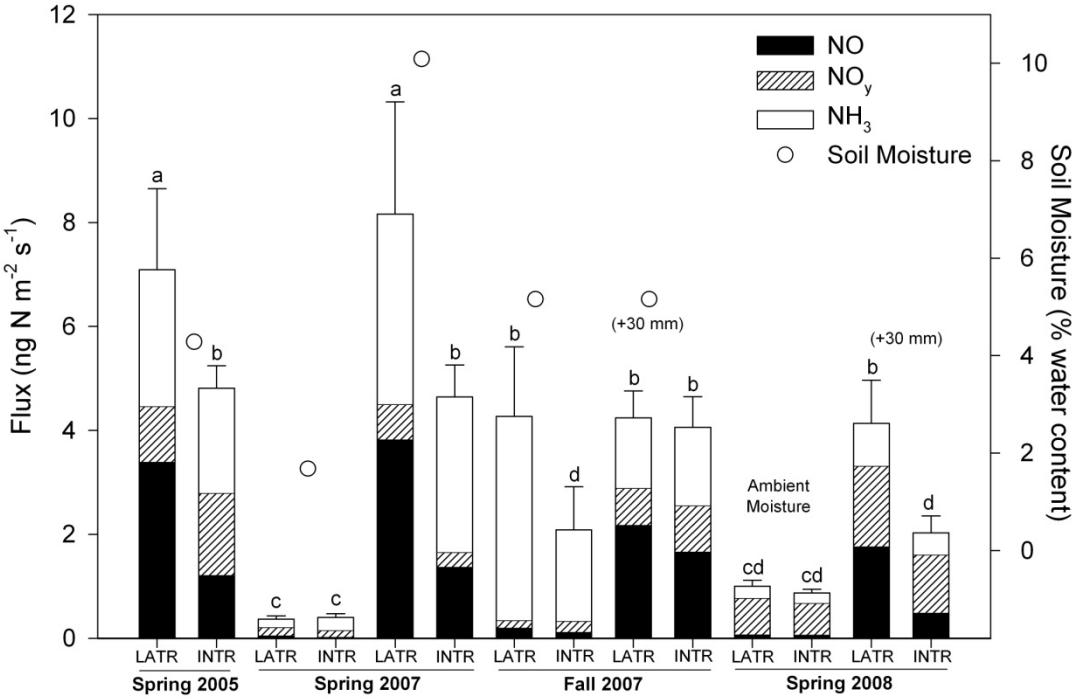


**Figure 4.3** Average daytime reactive N gas fluxes and soil moisture conditions during spring/fall growing season sampling periods, LATR = *L. tridentata*, INTR = interspace (2005: n = 9 for *L. tridentata* and n = 26 for interspace, Spring 2007: under ambient moisture n = 24 for *L. tridentata* and n = 68 for interspace, following irrigation n= 6 for *L. tridentata* and n = 14 for interspace, Fall 2007: under ambient moisture n = 9 , following irrigation n = 12, Spring 2008: under ambient moisture n = 27 for *L. tridentata* and n = 63 for interspace, following irrigation n = 12). Soil moisture content is based on neutron probe data from NDFF during the sampling periods, additional moisture resulting from localized irrigations are indicated above the background soil moisture content (eg. +30 mm indicates application of an additional 30 mm of water), soil moisture data was not available in the spring of 2008 and for these dates notes above bars indicate ambient and post-irrigation soil conditions. Letters indicate significant differences in total reactive N gas efflux ($p < 0.05$).

very wet spring of 2005, an El Ninõ year that produced high N loss rates, to those made during the extremely dry spring of 2007, a year when there was no spring germination of annual plants and N gas emissions were minimal. The highest N emissions were observed when soil moisture content was high, either as a result of natural precipitation patterns or following irrigation events. During these periods of high soil N gas efflux there was often, but not always, a significant effect of plant cover type, with the highest fluxes occurring in soils beneath *L. tridentata*. The composition of the total reactive N gas flux also varied considerably during the growing season. Nitric oxide was an important component of soil emissions during springtime high moisture conditions; however, during wet fall conditions and the dry spring soils of 2007 and 2008, NO was <10% of the total N flux. Ammonia often dominated growing season N loss with maximal $NH_3$ efflux of approximately 3 ng N $m^{-2}$ $s^{-1}$ occurring in the fall of 2007 and following irrigation in spring 2007. During these periods, $NH_3$ was 90 and 50% of total reactive N flux, respectively. Calculated daily N gas flux rates ranged from 0.09 mg N $m^{-2}$ $day^{-1}$ during the extremely dry spring of 2007 to 0.17 mg N $m^{-2}$ $day^{-1}$ during the wet El Ninõ spring of 2005 (Table 4.1).

Measurements collected during a 72-hour dry down period following a 10 mm artificial rain event showed a large pulse of reactive N gases that lasted for several days after precipitation (Figure 4.4). Following water addition, an augmented diurnal pattern in N losses was observed, with the magnitude of the midday value declining as soils dried out over several days. Nitrogen emissions were substantial the first day following precipitation; integration of the diurnal flux pattern estimated a total reactive N loss rate of 2.1 mg N $m^{-2}$ $day^{-1}$. Integration of the diurnal flux pattern for subsequent days shows that N emissions decreased 30% on the second day and an additional 50% the third day. Extrapolation of this decline in daily N loss with soil drying suggests

that by the 5th day emissions returned to the dry soil N loss rate of 0.06 mg N $m^{-2}$ $day^{-1}$. In total, the 4-day period of elevated N fluxes following a 10 mm rain event produced an additional 3.2 mg N $m^{-2}$ of reactive N gases (Table 4.2).

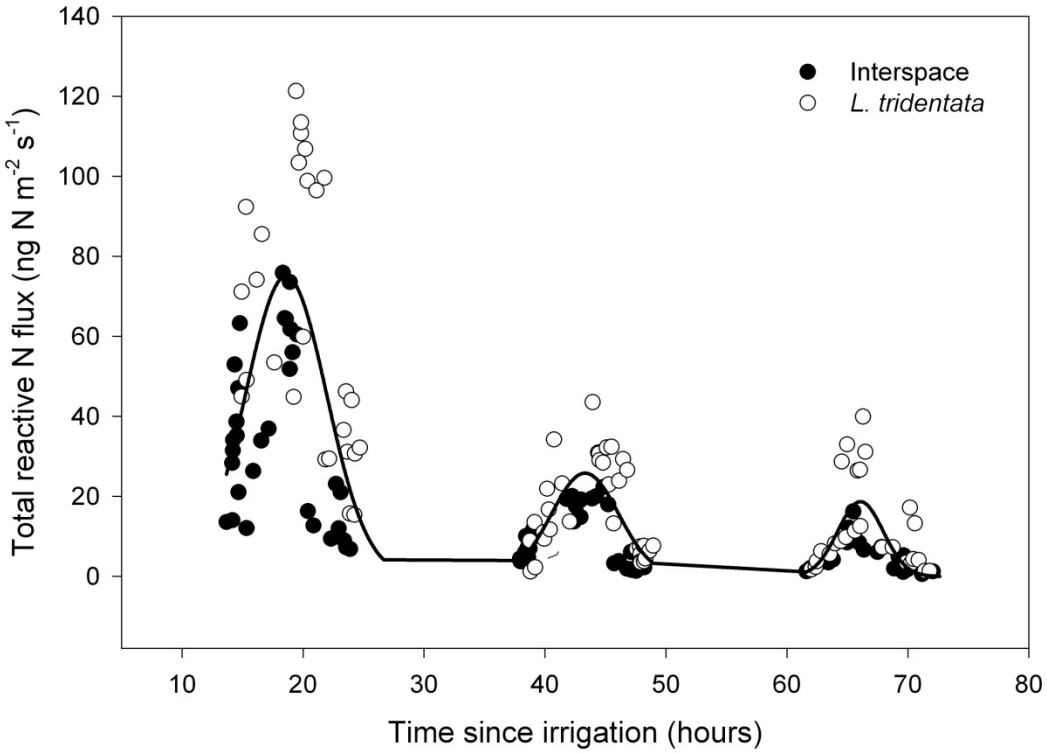


**Figure 4.4** Diurnal pattern in total reactive N gas efflux following a 10 mm artificial rain event during the summer (Day 1 $R^2 = 0.38$, $p<0.0001$, Day 2 $R^2 = 0.55$, $p<0.0001$, Day 3 $R^2 = 0.43$, $p<0.0001$).

The magnitude of total reactive nitrogen gas efflux associated with summer precipitation events increased with event size (Figure 4.5). All rain event sizes, even those as small as 1-2 mm, resulted in periods of elevated N gas emissions and, in general, larger rain events yielded larger pulses of N. Reactive N gas efflux immediately following 1-2 mm events were small, averaging 5.4-7.5 ng N $m^{-2}$ $s^{-1}$, and returned to dry soil rates within 24 hours. Flux rates were considerably larger immediately following 8-10 mm events, with fluxes averaging 20-34 ng N $m^{-2}$ $s^{-1}$ and 37-85 ng N $m^{-2}$ $s^{-1}$ in interspace and *L. tridentata* soils, respectively. Nitrogen gas losses following large events (25-30 mm) were considerably more variable, with the

**Table 4.2** Pulses of reactive N gases following different sized rain events and predicted post-rain N losses based on the 11-year summer (June-September) precipitation record for the NDFF.

| | *Rain Event Size (mm)* | | | | | |
|---|---|---|---|---|---|---|
| | 1-2 | 2-5 | 5-10 | 10-20 | >20 | |
| | *Total reactive N Flux (mg N $m^{-2}$)* | | | | | |
| | 0.21 | 1.69 | 3.17 | 4.59 | 6.00 | *Total Flux* |
| *Hydrologic Year* | *Number of Events* | | | | | *(kg N $ha^{-1}$)* |
| 1996-1997 | 2 | 1 | 1 | 0 | 3 | 0.233 |
| 1997-1998 | 2 | 1 | 2 | 1 | 3 | 0.310 |
| 1998-1999 | 4 | 2 | 1 | 0 | 3 | 0.134 |
| 1999-2000 | 2 | 2 | 1 | 0 | 0 | 0.070 |
| 2000-2001 | 1 | 2 | 1 | 0 | 0 | 0.068 |
| 2001-2002 | 3 | 0 | 0 | 0 | 0 | 0.006 |
| 2002-2003 | 0 | 1 | 2 | 1 | 1 | 0.186 |
| 2003-2004 | 1 | 1 | 1 | 1 | 0 | 0.097 |
| 2004-2005 | 1 | 2 | 2 | 1 | 0 | 0.145 |
| 2005-2006 | 2 | 2 | 0 | 0 | 0 | 0.038 |
| 2006-2007 | 0 | 0 | 8 | 0 | 1 | 0.314 |
| **Average** | **2** | **1** | **2** | **0** | **1** | **0.145** |

largest N losses occurring 36-48 hours after an artificial rain event in 2008 when average daytime fluxes were 82±18 and 140±32 ng N $m^{-2}$ $s^{-1}$ in interspace and *L. tridentata* soils, respectively. Comparable N losses were measured after a large irrigation in 2005; however similar irrigations in 2006 and 2007 yielded much smaller N loss rates of approximately 15- 20 ng N $m^{-2}$ $s^{-1}$. Post-rain pulses of reactive N gases ranged from 0.2 mg N $m^{-2}$ for small (1-2 mm) rain events to 6 mg N $m^{-2}$ for large (>20 mm) rain events (Table 4.2). Across an 11 year period of the NDFF precipitation record, summer rain events yielded an average reactive N gas loss of 0.145 kg N $ha^{-1}$;

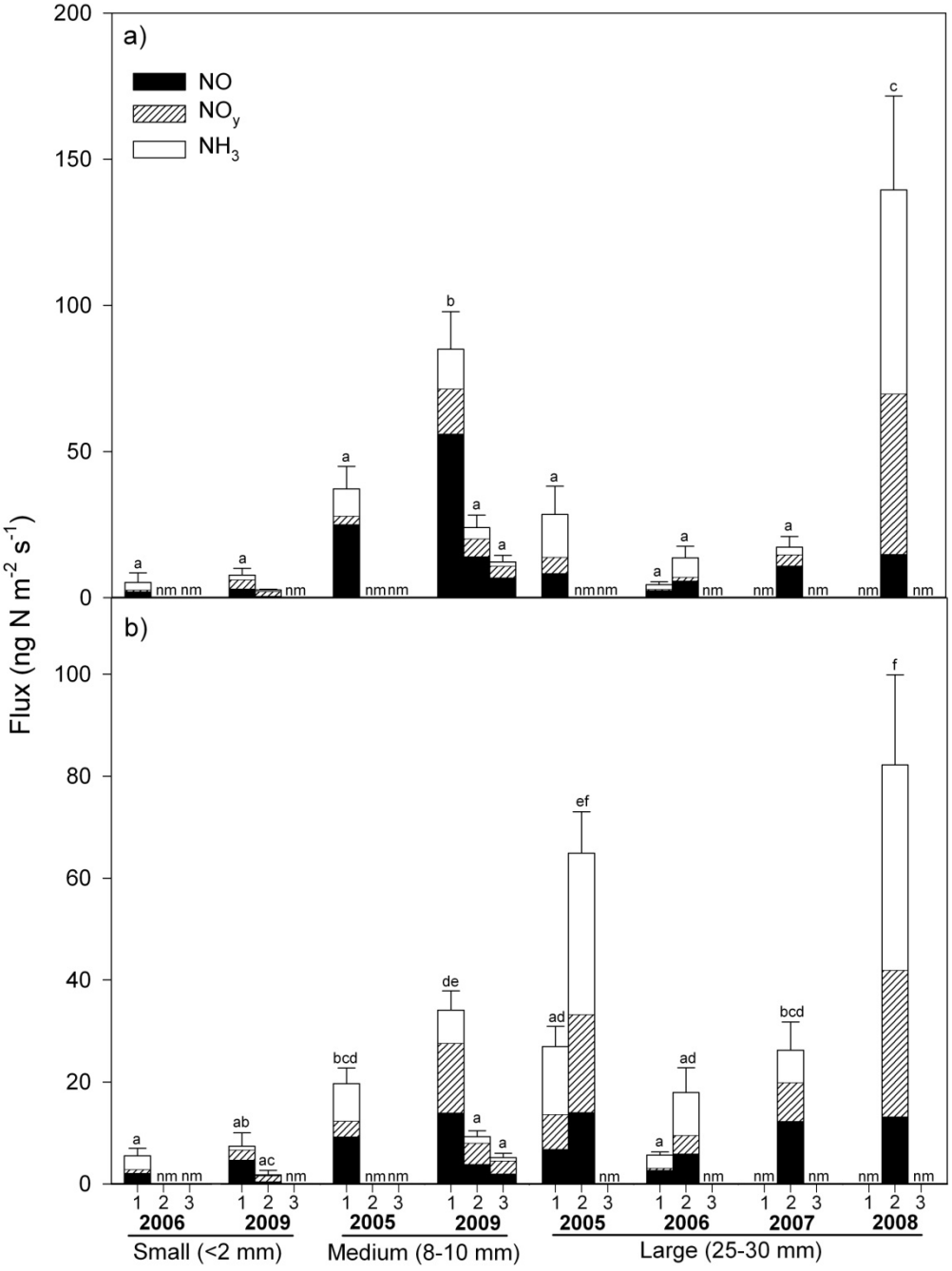


**Figure 4.5** Reactive N gas pulses across three days following different sized natural and artificial summer rain events (1 = 0-24 hrs, 2 = 24-48 hrs, 3 = 48-72 hrs post-irrigation) in **(a)** *L. tridentata* soils (small event sizes n = 3 in 2006 and n = 6 in 2009, medium events n = 5 in 2005, n = 31 in 2009, large events n = 3 in 2005, n = 4 in 2006, n = 17 in 2007, n = 13 in 2008) **(b)** interspace soils (small event sizes n = 11 in 2006 and n = 7 in 2009, medium events n = 8 in 2005, n = 33 in 2009, large events n = 9 in 2005, n = 9 in 2006, n = 27 in 2007, n = 13 in 2008). Letters indicate significant differences in total reactive N gas efflux within a cover type ($p < 0.05$), nm = not measured.

however wet summers produced more than double this flux and the extremely dry summer of 2002 had only 0.006 kg N $ha^{-1}$ of post-rain gaseous N efflux (Table 4.2).

Annual loss estimates for dry (< 50% of average precipitation) to very wet (> 200% of average) years were 0.1-0.6 kg N $ha^{-1}$ $yr^{-1}$ (Table 4.1). Across all scenarios, winter losses were the smallest, ranging from 0.005 - 0.01 kg N $ha^{-1}$ $yr^{-1}$. Spring/fall losses were larger and more variable, with a 10-fold range in N efflux from 0.02 kg N $ha^{-1}$ $yr^{-1}$ during a below average precipitation year to 0.2 kg N $ha^{-1}$ $yr^{-1}$ during a very high precipitation year. Annual losses during the summer were 0.07 kg N $ha^{-1}$ $yr^{-1}$, with pulses of an additional 0.006 – 0.3 kg N $ha^{-1}$ $yr^{-1}$ following precipitation.

**Discussion**

Annual losses of reactive N gases from the Mojave Desert depend on the amount and timing of precipitation and range from about 0.1-0.6 kg N $ha^{-1}y^{-1}$ (Table 4.1). For the entire Mojave Desert this represents the release of approximately 0.6-4 x $10^{-3}$ Tg N $y^{-1}$ of reactive N gases including both nitrogen oxides and $NH_3$ into the atmosphere. This compares to a global estimate of 21 Tg N $y^{-1}$ of $NO_x$ emissions from soils, 0.5 Tg N $y^{-1}$ of which are attributed to arid and semi-arid ecosystems (Davidson and Kingerlee 1997). Comparison of this N loss term with other aspects of the N cycle in the Mojave Desert indicates that this is a biologically relevant flux, Rundell and Gibson (1996) working at a similar site in the Mojave Desert estimated plant total exogenous N inputs to be 2-3 kg N $ha^{-1}$ $y^{-1}$ with 1-2 kg $ha^{-1}$ $y^{-1}$ entering as wet and dry deposition and the rest as fixation. This suggests that, depending upon hydrological conditions and variation in total inputs, 4-30% of exogenous nitrogen is lost as gas each year.

The considerable range in annual gaseous N losses is driven primarily by inter-annual variability in summer precipitation and in growing season moisture conditions. Summer fluxes, both from wet and dry soils, dominated annual N gas loss, encompassing 65-75% of the yearly flux in all climate scenarios. With the exception of extremely dry years, summer rain events stimulated approximately 50% of annual N gas emissions. Growing season soil moisture was also an important variable in determining annual N gas loss, with emissions ranging from 0.02-0.21 kg N $ha^{-1}$ across dry to very wet growing seasons. In contrast, winter months have a minimal influence on annual N gas emissions, contributing <5% to the annual N loss budgets under all precipitation scenarios. Overall, seasonal differences in the response of N fluxes to changes in moisture conditions were a defining characteristic of annual variability in soil N efflux in the Mojave Desert. This pattern is of particular importance to annual budgets in this ecosystem where across years, summertime precipitation ranges from 70% of total precipitation to as little as 10% (Blainey et al. 2007).

From the perspective of understanding the impacts of climate change on aridlands, these results suggest that predictions of future rises in global temperatures and regional alterations in precipitation pattern could have lasting impacts on gaseous N loss pathways. Strong diurnal peaks in N gas efflux support previous work showing that temperature is an important variable in describing N gas losses (McCalley and Sparks 2009), meaning that a several degree rise in temperature could yield a corresponding increase in daily N gas emissions. For our site in the Mojave Desert, changes in temperature that increase the number of days spent under summer as opposed to growing season temperature conditions could increase losses by as much as 0.05 mg N $m^{-2}$ $d^{-1}$. This study also highlights the importance of the timing and amount of precipitation in determining annual N emissions from desert soils, showing

the impacts of both growing season and summer moisture conditions on reactive N gas efflux. Our results support the hypothesis that the largest impact of climate change on arid regions could result from precipitation changes. For example, addition or subtraction of a large summer rain event (>20mm) will change annual N gas emissions by 0.06 kg $ha^{-1}$, representing a 10-60% change in annual reactive N gas efflux.

The magnitude of annual N gas efflux we report for the Mojave Desert is consistent with other estimates from arid and semi-arid regions. These range from 0.15-0.38 kg N $ha^{-1}$ $y^{-1}$ (Hartley and Schlesinger 2000) and 0.02-0.16 kg N $ha^{-1}$ $y^{-1}$ (Barger et al. 2005) in the Chihuahuan and Colorado Plateau deserts to 0.35-0.61 kg N $ha^{-1}$ $y^{-1}$ (Feig et al. 2008) and 1.4-1.6 kg N $ha^{-1}$ $y^{-1}$ (Otter et al. 1999) in semi-arid savannahs. The Mojave Desert has low annual precipitation relative to these other sites and on average 60% of this rainfall happens during the winter where it has little direct impact on soil emissions. We would therefore expect that N gas efflux from Mojave Desert soils would fall at the low end of estimates for arid and semi-arid regions; however, our annual estimate is similar to or larger than losses generated from higher precipitation sites. These differences are likely due to two factors, the inclusion of $NO_y$ and $NH_3$ in our estimate and the use of a wide range of moisture conditions to generate an estimate representative of both high and low precipitation years. We found that <50% of the total reactive N flux was NO, suggesting that if a similar combination of biotic and abiotic sources drive soil N emissions in other arid and semi-arid systems, then total reactive N efflux could be as much as double the annual NO fluxes reported in the literature. Second, arid and semi-arid ecosystems are characterized by highly variable precipitation regimes and inclusion of these natural extremes yields a large range in the magnitude of annual soil emissions. Therefore, calculations of annual N gas efflux based on measurements made within a single year

have the potential to substantially over or under estimate average losses and do not fully represent the range of N emissions typical of these ecosystems.

Our observations provide mechanistic information concerning N loss dynamics in arid ecosystems including the significance of daily, seasonal, and post-rain patterns in soil emissions. Daily N flux patterns are driven by the temperature dependence of both biotic (Skiba et al. 1993, Ludwig et al. 2001, Parton et al. 2001) and abiotic processes (Schlesinger and Peterjohn 1991, McCalley and Sparks 2009) and have been documented in other systems. Hartley and Schlesinger (2000) noted diurnal patterns of NO efflux during the summer in the Chihuahuan Desert; however in most soils this pattern was only evident when moisture was high. The dependence of daily patterns in NO efflux on moisture conditions has also been reported in a tropical savannah ecosystem where strong diurnal patterns were only observed during the rainy season (Johansson et al. 1988, Johansson and Sanhueza 1988). It has been widely suggested that the positive relationship between temperature and NO efflux documented in many ecosystems (Anderson and Levine 1987, Martin et al. 1998, Otter et al. 1999, Martin et al. 2003, Feig et al. 2008, Gelfand et al. 2009) breaks down under extreme moisture and/or temperature conditions that inhibit biological activity (Ludwig et al. 2001). In contrast, our work in the Mojave Desert shows that extreme temperature variations in dry summer soils can yield 8-fold changes in soil emissions across a single day and that these patterns, although smaller in magnitude, are also evident during dry periods in the winter and spring. In these desert soils, abiotic as well as biotic processes contribute to gaseous N loss, both of which are sensitive to temperature, likely explaining the persistence of diurnal patterns in N efflux across temperature and moisture conditions.

Most ecosystems also exhibit seasonal variation in N gas emissions associated with patterns in temperature and precipitation. Multiple studies show that in deserts

with a pronounced summer monsoonal system, a disproportionate amount of annual N loss occurs during this hot/wet period (Martin et al. 1998, Hartley and Schlesinger 2000, Barger et al. 2005). A similar pattern is documented in tropical forest and savannah sites where higher daily N gas emissions occur in the wet season than in the dry season (Davidson et al. 1991, Davidson et al. 1993, Otter et al. 1999, Kirkman et al. 2001, Feig et al. 2008). The seasonality of N gas loss is different where precipitation mostly occurs during cooler months. For example, Gelfand et al. (2009) show that in semi-arid shrublands in Africa the highest N losses occur during the warmest months of the year despite low soil moisture content, while wet, winter months exhibit the lowest N gas fluxes. In the Mojave Desert, seasonal patterns are linked to the timing of precipitation, which varies considerably across years, but often occurs predominantly during the cold winter months (Blainey et al. 2007). As seen in other systems, winter months are a minor source of N emissions even when moisture is high. In contrast, the combination of high temperature and precipitation in the summer produces maximal rates of N gas efflux; however, the frequency of such events is highly variable across years.

Pulses of N gases following precipitation, particularly during dry seasons, can be a substantial component of annual N emissions in many ecosystems, including the Mojave Desert (Davidson et al. 1991, Martin et al. 1998, Smart et al. 1999, Kirkman et al. 2001, Galbally et al. 2008). Post-rain N losses are typically described as a single peak in emissions immediately following soil wetting, with elevated fluxes returning to baseline levels over a time period of hours (Barger et al. 2005) to days (Scholes et al. 1997). In contrast, our study showed a pattern of post-rain N emissions composed of a series of declining diurnal cycles as soils dried, with the time to return to background levels predicted to range from 1-5 days depending on the size of the rain event. Hartley and Schlesinger (2000) suggested a similar multiday diurnal pattern

occurs following precipitation in the Chihuahuan Desert, however they only measured fluxes for 36 hours following precipitation. Summer precipitation is so variable in the Mojave Desert that based on recent climate data total post-rain N losses can range from 0.006 to 0.3 kg N $ha^{-1}$, meaning that during high precipitation summers, post-rain emissions are 3x higher than the re-wetting pulses of NO reported for seasonally dry tropical forests (Davidson et al. 1991) and greater than total annual losses reported for other North American deserts (Hartley and Schlesinger 2000, Barger et al. 2005); however, during other years summer rainfall is a trivial component of annual N losses.

The combination of daily, seasonal and annual drivers in N gas efflux highlight the importance of quantifying natural sources of variability when studying N loss processes in arid ecosystems. Analytical approaches that integrated these mechanistic drivers into budget calculations enabled us to not only generate a detailed estimate of reactive N gas emissions from the Mojave Desert, but to identify the sensitivities of this loss term to environmental changes. Given the uncertainties in how environmental conditions will shift under future climate change (Solomon et al. 2007), this approach enables us to explore trajectories of N loss dynamics under projections put forth by multiple climate change models.

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